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PREFACE

A new feature of the present volume is a comprehensive index of this and all previous volumes. Because of the varied character of physical chemistry, a given volume can cover only a part of the whole field. However, the practice of inviting a new author each year to cover a particular topic results in a wide coverage over the years, as is evident from the index.
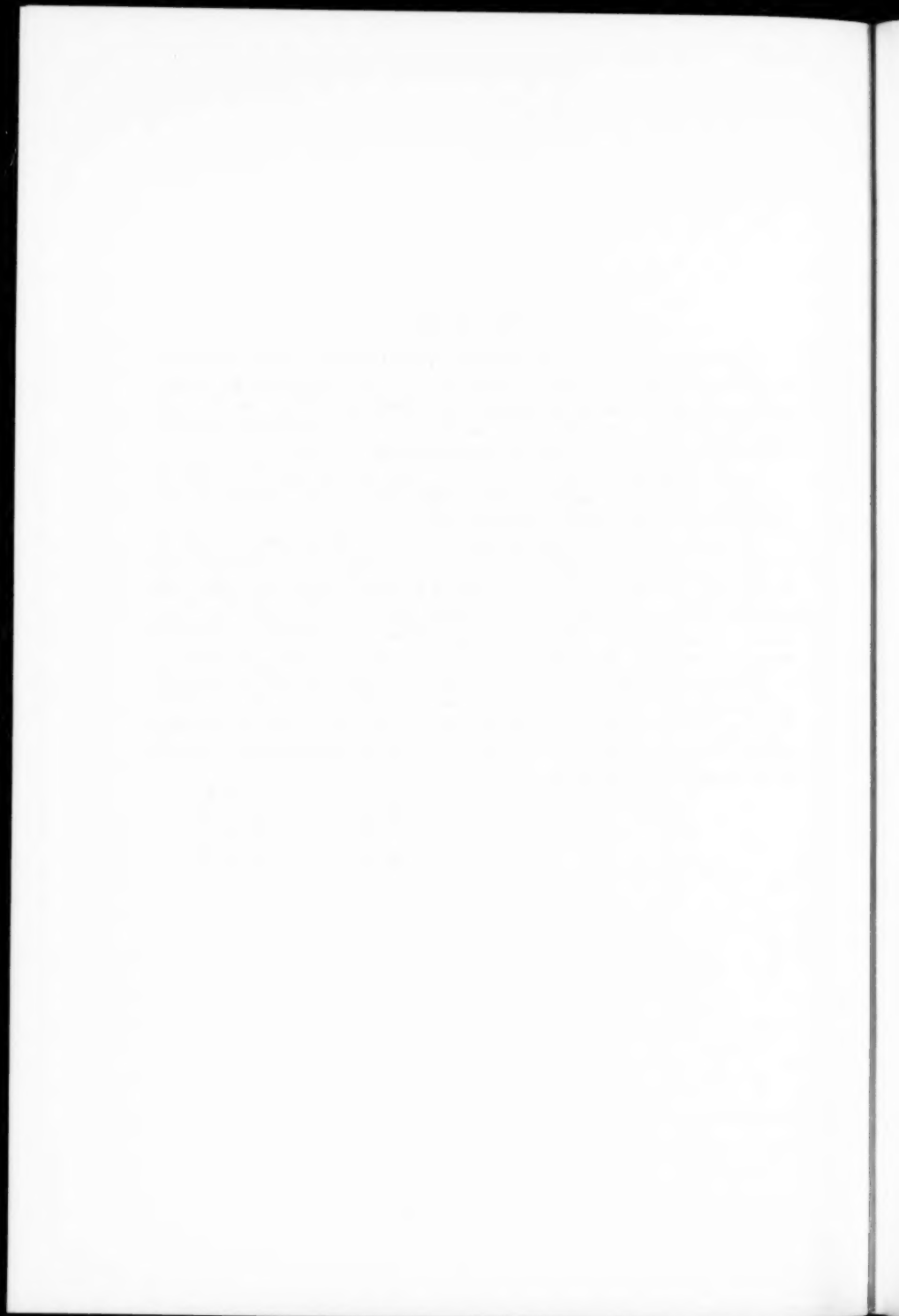
Again we are fortunate in having an outstanding group of scholars as authors of the various topics in this volume, and we feel sure the readers will appreciate their generous unpaid service.

The treatment here of fused salts is an indication of the current emphasis on high temperature chemistry, as is also the chapter on combustion and flames. Other chapters treat new aspects of frequently recurring topics. It is intended that the reviews shall in general deal critically with significant aspects of important fields rather than attempt an exhaustive uncritical listing of references. We hope we have been successful in our objective.

We are especially fortunate in having Miss Lois Cox helping both editorially and with the many other problems of getting this volume into print. Dr. Donald Kupke has again compiled the subject index. For the generous help of the authors and all others who have assisted us with this Review this year, we express our deep appreciation.

J. B.   J. D. F.
C. J. C.   D. F. H.
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H. E.   J. E. M.

CONTENTS

THERMOCHEMISTRY AND THERMODYNAMIC PROPERTIES OF SUBSTANCES[1]

By John P. McCullough

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One hundred nineteen years after Clausius announced, perhaps with unwarranted bravado, that "Die Energie der Welt ist konstant; die Entropie der Welt strebt einem Maximum zu," and 53 years after Nernst appended a third to the two laws of thermodynamics, chemists and a few essentially chemical physicists flooded the scientific literature with hundreds of papers based ultimately, if remotely, on the work of cannon-borers like Rumford and brewers like Joule. Sprung from engineering considerations of heat engines, the science of thermodynamics now includes concepts of extraordinarily broad ranges of validity and utility. Because of the wide applicability of thermodynamics in solving problems of so many kinds, reported work in this field increases yearly. Most present-day research in chemical thermodynamics seems far removed from the problems that concerned pioneer thermodynamicists like Carnot, who tried to understand limitations on the efficiency of heat engines. Nevertheless, a significant portion of the thermodynamic research reported in 1959 was stimulated by the need for better heat engines—but, in this age, heat engines that will allow man to explore the space beyond "der Welt" to which Clausius restricted himself. Thermodynamic and thermochemical studies of rocket propellants and their combustion products will swell the literature even more in coming years, for thermodynamic considerations provide the most realistic way of winnowing from the multitude of possible energy sources those few that will do the job.

This review necessarily is restricted and will be inadequate, on the one hand, for those readers who would like to see the entire field of chemical thermodynamics covered and, on the other hand, for those who would prefer a review in depth of one or a few significant topics. Because yearly summaries of published thermodynamic information have proved so useful to workers in the field, the tabulations featured in most previous reviews of this series are included. In addition, a few topics of general interest or of special interest to this reviewer are discussed briefly.

[1] This review covers recent publications on thermochemistry and chemical thermodynamics that were available to the reviewer in the original or as abstracts before December 1, 1959.

[2] Contribution No. 87.

THERMODYNAMIC AND THERMOCHEMICAL DATA

SUMMARIES OF PUBLISHED DATA

With a format similar to those in recent reviews on this subject, Tables I and II summarize the voluminous information published in the last year on thermodynamic properties of substances. Listed in these tables are the compounds for which thermodynamic data were reported, the properties reported, and literature citations. Only well-defined chemical compounds are included in the tabulations. Alloys or other physical mixtures, non-stoichiometric compositions, and substances in solution were excluded with regret. The thermodynamic properties considered are given in the footnote to Table I. Properties a to p and uv are experimentally determined or derived from experimental data by using standard thermodynamic relationships; properties q to t refer only to values in the ideal gas state, usually calculated by the methods of statistical mechanics.[3] The arrangement of inorganic substances in Table I follows the system of N.B.S. Circular 500 (257). In Table II, single organic substances are listed alphabetically by name, followed by groups of substances, also listed alphabetically.

Table III lists chemical reactions for which the heats and/or reaction equilibria were determined. This tabulation also is restricted to reactions between well-defined chemical species and excludes reactions in solution if solvent effects are significant.

DISCUSSION

So interrelated are the various disciplines of physical science that progress or discoveries in one area always are accompanied by related advances in other areas. Although many of the more important scientific discoveries have come from uninhibited exploration of the unknown, it is a fact that most research efforts, fundamental as well as applied, are directed by considerations of mankind's immediate and predictable material requirements. Thermodynamic researches described in the past year reflect both the interrelationship of progress in all fields of science and the directing influence of material needs. At the risk of slighting some research of fundamental thermodynamic importance—such as West's definitive study of elemental sulfur (335)—a few developments related to broad scientific and technological trends will be mentioned.

Materials and energy sources always have been among man's primary physical needs. Until recent years these requirements were met by using substances that could be obtained with relative ease from natural sources. In the past decade or so this picture has changed markedly. As a direct result of the need for radically new materials to allow man to do radically new things, the researches summarized in Tables I, II, and III involved most elements of the periodic table and many exotic combinations of them.

Stimulated by rapid developments in the field of electronics and pressing

[3] Many of the papers that report values of *abfgl* also give values of *qrst* for the solid and liquid states.

demands for further advances, intense research activity is in progress in the field of solid state physics. Heat-capacity studies at very low temperatures of elements such as Si, Ge, and Ga are yielding fundamental information about the nature of semiconductors, and similar studies of other substances (181, 182, 186, 233, 248, 271, 307) advance knowledge of the solid state in general.

The development of nuclear energy sources, high-speed aircraft, and missiles has created a voracious demand for new materials and fuels; chemically, the search for them covers the entire periodic table. Inspection of Table I shows that much effort has been placed on thermodynamic studies of rare earths of both series 4f and 5f, the transition metals, and other "rare" elements, none of which was of much practical importance two decades ago. Kelley's and Montgomery's comprehensive reports on titanium (148, 149) and samarium (211) compounds are notable contributions in the inorganic field.

Needs for new materials also extend to organic substances, particularly those that may be used at the high temperatures characteristic of modern machines. The aromatic complexes of metals—the "sandwich" compounds —are materials of great potential value and unusual theoretical interest, but only a little attention has been given to thermodynamic studies of this really new class of chemical compounds (56, 89).

Organic fluorine compounds comprise another promising class of chemicals with unusual properties. Commercial application of organic fluorine compounds, except as aerosols and refrigerants, has been slower than expected a few years ago, but part of the lag has been due to lack of fundamental knowledge about the organic and physical chemistry of such substances. Thermodynamic studies reported in the past year will help (72, 103, 228, 308), but more research clearly is needed. A real deterrent to any kind of physicochemical research on fluorochemicals continues to be the scarcity of suitably pure samples with which to work.

As noted in the introduction, the search for high-energy fuels has stimulated much thermodynamic research and, in the process, has opened up new vistas in high-temperature chemistry. Thus, Table I lists many substances that are important only at high temperatures—HO_2, aluminum monohalides, alkali halide ions, and the like. Also, calculations and determinations of thermodynamic functions now are being extended to temperatures well over 1000°K. (5, 8, 17, 164, 184, 236, 238, 242). Much of the work on boron compounds must stem in part from the value of this element as an ingredient of high-energy fuels.

One cannot help noting that the familiar chemical H_2O still is the subject of more published reports than any other compound.

SPECIAL TOPICS

CORRELATIONS, COMPILATIONS, AND REVIEWS

Although the number of possible chemical substances may be less than infinite, the impossibility of making detailed thermodynamic studies of all the compounds of interest is obvious. For this reason, one objective of ther-

TABLE I

Thermodynamic Properties Measured or Calculated Inorganic Compounds

Compound	Property[*]	Reference
Air	p	(243, 272, 329)
O, O₂	p	(126, 329)
O₂, O₃⁺	qrstuv	(17)
H	qv	(164)
H₂	kpq	(18, 19, 126, 164, 204, 222, 399)
D₂	kp	(18, 19, 204, 339)
HD	kp	(18, 19, 339)
T₂	k	(339)
HO, HO₂, DO, DO₂	u	(107)
H₂O	abcpn	(10, 127, 128, 249, 250, 258, 263, 283, 285, 289, 328, 330, 331)
D₂O	iklmp	(338)
⁴He	ip	(7, 8, 19, 23, 126, 324)
⁴He	blp	(32, 101, 116, 226)
A	u	(8, 205, 206, 224)
F	qat	(305)
Cl, Cl₂, HCl, ClF	b	(135)
ClO₂F	ahjl	(286, 291)
I₂	abdefg	(335)
S	ouv	(141)
H₂S, D₂S	ahijk	(96, 165, 166, 295)
Se	aik	(96, 295)
Te	hj	(347)
TeO₂	cp	(8, 126, 224, 259, 260, 261, 329)
N₂, N₂⁺, NO, NO⁺ NO, NO₂, N₂O	t	(175)
N₂O	cp	(224)
NH₃	pu	(126, 343)
NF₄	ikp	(52)
HNF₄	fikp	(252)
NO₂Cl	mu	(142)
NH₄IO₄	u	(318)
P₄O₁₀	qrsuv	(114)
(PNF₂)₃ and (PNF₂)₄	fghijk	(248)
Sb	a	(248)
BiCl	suv	(67)
BiCl₃	suv	(67)
BiI₃	ik	(63)

Compound	Property[*]	Reference
CdTe	mv	(74)
Cd₃P₂, Cd₃As₂, Cd₃Sb₂	u	(277)
CdSiO₃	aluv	(14, 152)
Hg	a	(295)
HgBr₂	ef	(134)
Cu	abg	(12, 20, 169, 182)
CuSO₄·3NH₃	u	(9)
Cu(CO)₃(OH)₂	ade	(93)
CuSb	a	(325)
Ag	a	(12)
AgNO₃	fg	(256)
Au	a	(248)
AuBr, AuBr₃	u	(281)
Pt	uv	(248)
cis- and trans-[Pt(NH₃)₂Cl₂]	a	(46)
(NH₄)₂IrCl₆	ad	(13)
Ru	al	(51)
Ni	a	(306, 323)
α-NiSO₄·6H₂O	a	(310)
Co	a	(320)
Fe	ah	(20, 39, 320, 323)
FeO₄	adl	(111, 313)
FeCl₂, FeCl₃	u	(160)
FeS	al	(112)
FeS₂(pyrite)	a	(313)
FeTe₄	al	(337)
FeSbr₂	uv	(97)
Fe(CO)₅	abjgiklmou	(59, 170)
CuFeO₄	al	(154)
CuFeS₂	a	(313)
MnCl₂	u	(160)
HMn(CO)₅	fik	(120)
Cr	h	(39)
Mo	al	(50)
MoO₂, MoCl₄, MoCl₅	u	(282)
MoO₂Cl₂, MoO(OH)₂Cl₂	u	(106)
W	al	(50)
WO₂	lou	(109, 180)
WO₃	hlou	(109, 180, 200)
W₄O₁₁, W₄O₄₈	lu	(109)
WCl₆	ik	(280)
ZnWO₄, NiWO₄	a	(346)

Compound	Property[*]	Reference
PrCl₃·nH₂O	al	(119)
Ce	defgn	(196)
CeF₃	afgh	(153)
CeS, CeS₃	aluv	(155)
24 Rare earth compounds	aluv	(210)
La₂O₃	aiu	(100, 344)
La(OH)₃	u	(344)
LaCl₃	hj	(219)
LaCl₃·nH₂O	al	(119)
LaCl₃, La₂(SO₄)₃, and La₂(SO₄)₃·9H₂O	u	(209)
Pu	de	(35)
PuF₄	u	(40)
PuF₆, NpF₆	a	(334)
U	a	(296)
U₄O₉	adl	(336)
α-UF₄, β-UF₄, UF₅, UF₇	uv	(1)
UCl₄, UCl₅	h	(137)
17 Uranium halides, oxides, nitrides, carbides	u	(179)
UC	fikuv	(33)
Th	ou	(87)
ThS₂	aluv	(296)
(BeO)ₙ, n = 1–6	j	(155)
BeF₂	fhijk	(49)
Be₂C	uv	(225)
Mg	hj	(240)
MgO	a	(294)
MgO, MgH, CaO, CaH, SrO, SrH, BaO, BaH	qrsv	(15, 171)
MgS	v	(326)
MgSO₄	dv	(64)
MgCd	adel	(70)
Ca	hj	(309)
Ca(OH)₂	aluv	(294)
CaSO₄	dv	(118)
CaSeO₄·2H₂O	uv	(70)
Ca(OH)₂·3CaPO₄, CaF₂·3CaPO₄, CaCl₂·3CaPO₄, CaTiO₃, CaTiSiO₃	u	(274)

Compound	Property	Reference	Compound	Property	Reference	Compound	Property	Reference
BiCl₃	suv	(67)	WCl₆	ik	(280)	CaCl₂·3CuPbO₃, CaTiO₃, CaTiSiO₅	u	(105)
BiI₃	ik	(63)	ZnWO₄, NiWO₄	a	(346)		uv	(317)

Left group

Compound	Property*	Reference
C(g), C(g)	qv	(164)
Carbon (misc. vapor species)	qrsu	(236)
CO	p	(329)
CO₂	cp	(126, 172, 188, 224)
(CS)x	u	(125)
Si	a	(91, 145, 232)
SiO₂ (vein quartz)	ad	(313)
SiF₄	abfg	(162)
Ge	a	(91, 136, 145, 183, 232)
GeH₄, GeH₆	ik	(6)
GeS	fhi	(299)
Sn	a	(232)
SnS₂, Sn₂S₃	v	(276)
Pb	g	(168)
PbF₆	hj	(218)
PbX₂(X = F, Cl, Br, D	fg	(24)
PbSiO₃	aluv	(14, 152)
PbSiO₄	al	(152)
12 Inter-Group IVB Compounds	q	(73)
Ga	a	(271)
GaS	ik	(300)
GaP	h	(92)
GaAs	hmv	(74, 92)
InP	hmv	(74, 92)
InSb	uv	(69, 74, 266)
Tl₂O₃	v	(265)
TlCl	alu	(16, 28)
TlS	ik	(157)
Tl₂SeO₄	uv	(273)
Zn	abgikl	(94)
Tl₂CO₃, Tl₂CS₃	ik	(78, 96, 169, 271, 304)
ZnCl₂	ik	(27)
ZnS	huv	(11, 64, 255, 301)
Cd	a	(295, 304)
CdCl₂	fghijk	(27)
CdS	h	(301)
CdSe	v	(74)

Middle group

Compound	Property*	Reference
Nb	hj	(303)
TiO₂(rutile)	a	(144)
TiF₄	uv	(25)
TiCl₄	iu	(140, 235)
TiOCl	uv	(264)
TiBr₃	uv	(115)
TiBr₄	u	(217)
TiI₄	qnstu	(138, 322)
ZnTiO₄	uv	(317)
FeTiO₄	uv	(149)
24 Titanium compounds	various	(148)
ZrO₂	d	(198)
HfF₄	ln	(143)
HfCl₄	hj	(47)
B₂O₃	u	(246)
B₆H₆	fik	(98)
BX₃(X=F, Cl, Br)	rst	(5)
BF₃	abfg	(162)
B₃F₄	fhik	(88)
BCl₃	u	(139)
[BaF₄((CH₃)N)₄]₄	f	(88)
TlB₃	uv	(163)
Al	aik	(12, 233, 245)
Al₂O₃	ajn	(102, 196, 197)
AlF	stu	(342)
AlX (X=F, Cl, Br)	rst	(5)
AlF₃	hjst	(319)
AlCo	ad	(100)
YₓO₆	al	(262)
Yb, Tm, Dy, Sm	j	(302)
Er	o	(302)
Er₂O₆	u	(302)
Gd	o	(302)
Sm	defgno	(196, 302)
Sm₂O₃	u	(302)
8 Samarium compounds	uv	(211)
Nd	defgno	(196, 302)
NdₓO₆	alu	(100, 302)
Pr	den	(196)

Right group

Compound	Property*	Reference
CaMn₃	hjuv	(294)
SnM(M = Si, Pb, Ge, Sn)	u	(213)
SrMoO₄, SrWO₄	a	(346)
BaC₂	u	(124)
BaMoO₄	a	(347)
10 Alkaline earth titanates	uv	(149)
MF, (MF)₂(M =Li, Na, K, Rb, Cs)	j	(80)
Li	ae	(186)
LiX(X=F, Cl, Br)	rst	(5)
LiCl	hj	(220)
LiClO₄	u	(185)
Li₂TiO₃	uv	(317)
Na	a	(307)
Na₂O₃	den	(43, 184)
NaF	ik	(225)
NaCl	a	(176)
NaBrO₃	u	(142)
NaNH₄	alv	(61)
NaIrCl₆·H₂O	ad	(13)
Na₂CrO₄	v	(132)
Na₂CrO₄, NaMoO₄, NaWO₄	fg	(231)
KCl	al	(46, 176, 311)
K₃IrCl₆	ad	(13)
K₂CrO₄, K₂MoO₄, K₂WO₄	fg	(231)
KMg₃AlSi₃O₁₀F₂	abfghuv	(147)
K₂O·23CaO·12SiO₃	u	(221)
Rb	a	(181)
RbF	fgin	(143)
RbNO₃	adelg	(215)
Ca	adf	(75)
20MₓX⁺ alkali halide ions	s	(208)
58 Gaseous monoxides	r	(34)
27 Intermetallic compounds of Groups I, II, and III	u	(22)

* Key to letter symbols for thermodynamic properties (Tables I and II)

a. C_p or C_{std} of solid
b. C_p or C_{std} of liquid
c. C_p of gas
 Transition temperature
 Heat of transition
 Triple point

g. Heat of fusion
h. Vapor pressure of solid
i. Vapor pressure of liquid
j. Heat of sublimation
k. Heat of vaporization
l. Entropy of solid or liquid
m. Entropy of gas
n. High-temperature enthalpy

o. Heat of combustion
p. Data of state
q. $F°-H°_0$ or $(F-H°_0)/T$
r. $H°-H°_0$ or $(H°-H°_0)/T$
s. $S°$
t. $C_p°$
u. $\Delta H_f°$
v. $\Delta F_f°$

TABLE II

THERMODYNAMIC PROPERTIES MEASURED OR CALCULATED
ORGANIC COMPOUNDS

Compound	Property*	Reference
Acetic acid	ou	(86)
Acetylene	qp	(30, 238, 333)
Benzene	p	(214)
bis-Benzenechromium	ou	(89)
Benzotrifluoride	abcfgiklmpgrstuv	(269)
n-Butane	cp	(66)
n-Butanol	p	(284)
Carbon tetrachloride	iklm	(121)
Cycloheptanone	o	(292)
Cyclopentane	ckmpqrstuv	(192)
1,1-Difluoro-2-chloro-2-bromoethylene	qrst	(316)
Difluorochloroethane (Freon-142)	ip	(45)
1,1-Difluoro-2,2-dibromoethylene	qrst	(223)
Difluorodichloromethane (Freon-12)	p	(239)
1-*cis*-3-Dimethylcyclopentane	ckmp	(192)
Dysprosium ethylsulfate	a	(54)
Ethane	cp	(41, 66, 224, 314)
Ethanol	cp	(285)
1-Ethyl-3,4-dinitropyrrole	d	(251)
Ethyl ether	p	(285)
meta-Fluorobenzotrifluoride	ikou	(103)
Fluoroethane	qrst	(42)
Furan	qst	(227)
n-Heptane	ip	(53, 214)
n-Hexane	p	(110)
Methane	cp	(41, 66, 126)
Methanol	cp	(285)
2-Methylbutane	p	(287, 288, 327)
2-Methyl-1-butene	qrstuv	(193)
Methylcyclopentane	ckmp	(192)
Methyl ether	qrst	(187)
Methylnitrate	u	(253)
2-Methyl-2-propanethiol	qrstuv	(270)
3-Methylthiophene	qrstuv	(270)
Nitrobenzene	b	(177)
n-Octane	i	(53)
Perfluoro-2-butyltetrahydrofuran	ckp	(345)
Perfluorocyclobutane	ip	(72)
Perfluoroethylcyclohexane	ikou	(103)
Perfluoro-*n*-heptane	ouv	(103)
Perfluoromethane	abdefg	(162)
Perfluoromethylcyclohexane	ikou	(103)
Polyethylene	a	(297)
Praeseodymium ethylsulfate	a	(202)
Propane	cp	(66, 224)

TABLE II (*continued*)

Compound	Property*	Reference
n-Propanol	p	(285)
Pyrrole	qst	(227)
Pyrrolidine	abcdefgiklmopqrstuv	(123, 191)
Succinic acid	o	(146)
Tetramethyllead	ikouv	(104)
2-Thiabutane	qrstuv	(270)
Thianthrene	o	(146)
3-Thiapentane	qrstuv	(270)
Thiophene	qst	(227)
Trifluoromethane	ipt	(129)
Trimethylgallium	fghijkou	(174)
2,2,4-Trimethylpentane	i	(53)
Uranium pentaethoxide	abdefgikl	(315)
Vinylidene chloride	abfgiklmqrstuv	(122)
22 Amines and anilines	p	(58)
6 Amino acids	o	(321)
7 Aromatic complexes of transition metals	hj	(56)
9 Aromatic compounds	h	(158)
37 Aromatic compounds	i or j	(275)
Benzene, pyridine, and 6 methyl derivatives	kp	(62)
3 Butylamines	ou	(84)
Butylpalmitate, -stearate, -oleate	hj	(247)
CH, CH_2, CH_3, CH_4, C_2H_2, C_2H_4	qv	(164)
5 Chloroalkanes, C_1–C_4	p	(188)
6 Dimethylpyridines	fgik	(60)
4 1,3-Dioxa- and 1,3,5-trioxacycloalkanes	ikou	(90)
12 Fatty acids	p	(57)
14 Fatty acids	cik	(26)
78 Halogen derivatives of CH_4 and C_2H_4	u	(190)
13 Metal alkyls	o	(167)
5 Methylhydrazyl radical ions	u	(71)
Miscellaneous organic compounds	t	(189)
Naphthalene, nitrobenzene, and phenol	ik	(291)
cis- and *trans*-Nitrosoisobutane dimers	o	(84)
3 Nitrotoluenes	fg	(29)
6 Normal paraffins	p	(195)
30 Organic compounds	fi	(194)
3 Organo-tin compounds	u	(229)
3 Polymers	ad	(298)
3 Polyphenyls	n	(332)
Polysulphones of 4 butenes	ou	(130)
n-Propyl-, *i*-propyl-, and phenylcyanide	ou	(85)
7 Rare earth ethylsulfates	a	(203)
4 Sodium palmitates	al	(340, 341)
13 Straight-chain primary amides	hj	(68)
cis- and *trans*-1,3,5-Trimethylcyclohexanes	suv	(77)
Zirconium tetra-*tert*-butoxide and tetra-amyloxide	i	(31)

TABLE III

Reaction Heats and Equilibria

Reaction	Reference
32 Reactions involving HO and HO_2	(107)
$(HF)_2 = 2HF$	(293)
$12F_2 + 3H_2SO_4 = 3SF_6 + 6HF + 4O_3$	(308)
$N_2O_4(g) = 2NO_2(g)$	(131)
$ClNO_2(g) + NO(g) = ClNO(g) + NO_2(g)$	(252)
$ClNO(g) + N_2O_5(g) = ClNO_2(g) + 2NO_2(g)$	(252)
$X_4(g) = 2X_2(g)$, $(X = P, As, Sb)$	(74)
$2Pb(l) + S_2(g) = 2PbS(s)$	(312)
$MOH(g) = M(g) + OH(g)$, $(M = Ga, In, Tl)$	(37)
$Tl(s) + AgCl(s) = TlCl(s) + Ag(s)$	(16)
$Tl_2Cl_2(g) = 2TlCl(g)$	(28)
$ZnS(s, \beta) + H_2(g) = Zn(s) + H_2S(g)$	(255)
$ZnS(s) + H_2(g) = Zn(g) + H_2S(g)$	(64)
$ZnAs_2 = \frac{1}{3} Zn_3As_2 + \frac{1}{3} As_4$	(178)
$Zn(NH_3)_2CS_2(s) = ZnS(s) + 2NH_3(g) + CS_2(g)$	(95)
$CdO(s) + H_2O(l) = Cd(OH)_2(s)$	(278)
$CuSO_4 \cdot 4NH_3 = CuSO_4 \cdot 3NH_3 + NH_3$	(9)
$CuSO_4 \cdot 4NH_3 = CuSO_4 \cdot 2NH_3 + 2NH_3$	(9)
$CuSO_4 \cdot 3NH_3 = CuSO_4 \cdot 2NH_3 + NH_3$	(9)
$Ni(NH_3)_3CS_2(s) = NiS(s) + 3NH_3(g) + CS_2(g)$	(95)
$Fe_2Br_4(g) = 2FeBr_2(g)$	(241)
$WO_3(s) + H_2O(g) = WO_3 \cdot H_2O(g)$	(201)
Free energy change of 8 reactions of the lower tungsten chlorides	(279, 280)
$TiF_4(g) + Hg(l) = \frac{1}{2} Hg_2F_2(s) + TiF_3(s)$	(25)
$TiI_2(g) = Ti(s) + 2I(g)$	(117)
Metallurgical reactions of titanium	(148)
$B_2H_6(g) + 6Cl_2(g) = 2BCl_3(g) + 6HCl(g)$	(139)
$B_5H_9(g) + 12Cl_2(g) = 5BCl_3(g) + 9HCl(g)$	(139)
$AlF_3(s) + 2Al(s) = 3AlF(g)$	(342)
$Al_4C_3(s) = 4Al(g) + 3C(s)$	(199)
$4MCl_3(s) + 3O_2(g) = 2M_2O_3(s) + 6Cl_2(g)$, $(M = Ce, La, Nd, Sm)$	(212)
$2UF_5 = UF_4 + UF_6$	(244)
$\frac{1}{3}Pu(l) + \frac{1}{4}UF_4(l) = \frac{1}{3}PuF_3(l) + \frac{1}{4}U(l)$	(40)
$Pu(l) + UF_3(s) = PuF_3(l) + U(l)$	(40)
Heat and free energy of 16 reactions of beryllium and tungsten oxides	(49)
$Mg + O = MgO$	(38)
$Mg + OH = MgOH$	(38)
$MgS(s) + H_2O(g) = MgO(s) + H_2S(g)$	(64)
$Ba(l) + CaCl_2(l) = BaCl_2(l) + Ca(l)$	(230)
$M_2(OH)_2(g) + N_2(OH)_2(g) = 2MN(OH)_2(g)$	
$\quad$ (M = Rb, K, Na, Na, K as N = Cs, Rb, K, Rb, Cs)	(268)
$2MOH(g) = M_2(OH)_2(g)$, $(M = Na, K, Rb, Cs)$	(268)
Dimerization of alkali halides	(79, 80, 207, 267)
$M^+(g) + MX(g) = M_2X^+(g)$, (alkali halides)	(48, 208)

TABLE III (*continued*)

Reaction	Reference
$Na_2BeF_4(l) = NaF(l) + NaBeF_3(l)$	(225)
Heats of 9 hydrogenation reactions	(290)
1,3,5-Trimethylbenzene(g) + 3H$_2$(g)	
= *cis*-1,3,5-trimethylcyclohexane(g)	(77)
1,3,5-Trimethylbenzene(g) + 3H$_2$(g)	
= *trans*-1,3,5-trimethylcyclohexane(g)	(77)
trans-1,3,5-Trimethylcyclohexane(g)	
= *cis*-1,3,5-trimethylcyclohexane(g)	(77)
$C_6F_{10}(CF_3)_2 + 8F_2 = 8CF_4$	(308)
$2C_4Cl_3F_7 + 3F_2 = 2C_4F_{10} + 3Cl_3$	(308)
$2C_4Cl_3F_7 + 9F_2 = 8CF_4 + 3Cl_2$	(308)
Heats of chlorination of hydrocarbons	(156)
Heats of bromination of organo-tin compounds	(229)
Butadiene-vinycyclohexane reaction	(133)
Di(methylcyclopentadiene)dedimerization	(99)
$xCH_2O(g)(1$ atm., $25°C.) = (CH_2O)_x(s)$	(65)
Isomerization equilibria of C_2H_6S, C_3H_8S, and $C_4H_{10}S$	(270)
alkane thiols and sulfides and the methylthiophenes.	
cis-Decahydronaphthalene = *trans*-decahydronaphthalene	(4)
cis-3,5-Dimethylcycloheptanone = *trans*-3,5-dimethylcycloheptanone	(3)
axial-Cyclohexanol = *equatorial*-cyclohexanol	(234)
axial-Chlorocyolohexane = *equatorial*-chlorocyclohexane	(161)
axial-Bromocyclohexane = *equatorial*-bromocyclohexane	(81)
trans-(CH$_2$X)$_2$ = *gauche*-(CH$_2$X)$_2$, (X = Cl, Br)	(216)
$CH_3ONO(g) + \frac{1}{2}O_2(g) = CH_3ONO_2(g)$	(253)
$CH_3ONO(g) + NO_2(g) = CH_3ONO_2(g) + NO(g)$	(253)
$C_2H_4(g) + H_2O(g) = C_2H_5OH(g)$	(55)
$2C_2H_5OH(g) = C_2H_5OC_2H_5(g) + H_2O(g)$	(55)
$CCl_3Br(l) + CH_2 = CHOCCH_3(l) = CCl_3CH_2CHBrOCCH_3(l)$ (with O double bonds)	(21)
49 Reactions of organic sulfur compounds	(82)

modynamic research often is to obtain fundamental information about molecular structure and energetics for use in estimating thermodynamic property values by theoretical or semi-empirical methods. Many articles describing methods of correlation and estimation are published each year. Some of these methods are based on sound theoretical concepts from molecular physics (but seldom applied quantitatively), and others are strictly empirical.

Allen has described in detail one of the most satisfactory semi-empirical correlations of the heats of formation of hydrocarbons and some hydrocarbon derivatives (2). His method correlates the heats of formation of hydrocarbons almost as accurately as they can be measured. Allen's approach can be

shown by the expression he used to correlate the heats of atomization, ΔH_A, for alkanes and cycloalkanes:

$$\Delta H_A = N_{CH}E(C\!-\!H) + N_{CC}E(C\!-\!C) + X\alpha(CCC) - Sa - T\beta(CCC)$$

where N_{CH} and N_{CC} are the number of C—H and C—C bonds in the molecule; $E(C\!-\!H)$ and $E(C\!-\!C)$ are *standard* values of thermochemical bond energy, assumed to be the same for all alkanes; $\alpha(CCC)$ is the interaction energy for pairs of next-nearest-neighbor carbon atoms and X is the number of such pairs; a is the *gauche-n*-butane interaction energy and S is the number of such interactions; and $\beta(CCC)$ is the trigonal interaction energy involving three carbon atoms, each of which is a next nearest-neighbor to the others, and T is the number of trigonal interactions. If enough experimental data are available, the correlation can be extended to compounds containing elements other than carbon and hydrogen. Allen's paper also may be recommended as a concise and complete survey of methods for correlating and estimating heats of formation of organic compounds.

Chemists and engineers who use thermodynamic data are not necessarily qualified to evaluate the often discordant information in the literature or to develop simple methods for estimating thermodynamic properties. For this reason, reports such as Edmister's extensive series *Applied Hydrocarbon Thermodynamics* (76) are especially valuable. Recent books by Reid & Sherwood (254) and by the late K. A. Kobe (159) also will be useful to those whose primary concern is with the application of thermodynamic data.

Specialized reviews of the thermodynamics of a particular class of chemical substances not only aid the working thermodynamicist by consolidating pertinent information on the chosen subject but also serve to emphasize areas where more research is needed. Some of the papers already mentioned are in the nature of reviews (148, 211). Also to be noted are those by Gray and co-workers on organic and inorganic azides (83) and hydroxyl and alkoxyl radicals (107, 108), and that of Patrick on fluorocarbons (228).

CONFORMATIONAL ANALYSIS

A little over 20 years ago thermodynamic methods were used to show the importance of restricted rotation about single bonds between polyvalent atoms. Since then, many investigations have been made of the forces hindering internal rotation and their effects on the stable molecular conformations of complex organic molecules. Although most early and many recent studies of internal rotation used the thermodynamic approach, investigations of vibrational spectra (42, 123, 161, 234), microwave spectra (173), dipole moments (216), and ultrasonic relaxation (44) have contributed much in the field of conformational analysis. Several articles included in this review report information on barriers to internal rotation and energy differences between molecular conformations. Many important investigations of internal rotation by microwave spectroscopy, which make possible better calculations of thermodynamic functions, are not reviewed here because Lin &

Swalen have just published a comprehensive review of this subject (173).

Studies of molecular conformation have been particularly important in gaining understanding of both the physical and the organic chemistry of cyclic compounds. Allinger's experimental studies of isomerization equilibria for decalins (4) and cycloheptanones (3) are important developments of the past year. Egan & Buss report studies of the equilibria in mesitylene hydrogenation that allowed them to determine the energy and entropy differences between *cis*- and *trans*-1,3,5-trimethylcyclohexanes (77). Their results confirm presently accepted ideas about the structural and energy relationships among methyl-substituted cyclohexanes.

Several recent papers described thermodynamic investigations of the conformations of cyclopentane and its derivatives. In 1947, Kilpatrick *et al.* introduced the concept of free pseudorotation to explain the properties of cyclopentane (151), but later spectroscopic work was interpreted as casting doubt on this concept. New and accurate thermodynamic studies of cyclopentane (192) and pyrrolidine (123, 191) removed this doubt conclusively. This recent work also showed that free or restricted pseudorotation is a general phenomenon occurring in compounds with saturated five-member rings. A theoretical paper by Pitzer & Donath discussed in detail the conformations and strain energy in cyclopentane and its derivatives (237). From estimates of the barriers hindering internal rotation about each of the five ring bonds, these authors calculated the barriers hindering pseudorotation in several derivatives of cyclopentane. Their calculated results agree with the few known values as well as can be expected. Awareness of the effects of conformational differences on reactivity has led to many advances in the organic chemistry of cyclohexane derivatives (81). Progress in the organic chemistry of cyclopentane derivatives also may be stimulated by better understanding of conformational effects, as discussed in a recent paper by Brutcher *et al.* (36).

Apparatus and Techniques

Continuing advances in experimental methods are necessary for progress in thermodynamics and thermochemistry. Many of the papers cited in this review describe new techniques that will be useful to other workers. However, extension of thermodynamic research to new substances and new extremes of temperature, as discussed in a foregoing section, requires radically new experimental techniques, and really new ideas are not common. Adiabatic calorimetry can be pushed to 1000°C. with reasonable accuracy [Stansbury (306)], and although attempts to push drop calorimetry to much higher temperatures are in progress, the upper temperature limit still is too low. Non-calorimetric methods also are available or under development. For example, the marriage of the Knudsen effusion cell and high-temperature mass spectrometer has been very fruitful (48, 49, 69, 73, 74, 241, 267, 268). Electron impact studies (71) and flame photometry (37, 38) also have yielded valuable information about radicals and other high-temperature

chemical species; and the shock tube (272) holds promise if the results are interpretable.

In thermochemistry, moving-bomb calorimetry has been thoroughly established [Good *et al.* (103, 104)], and many such calorimetric systems are under construction at the present time. The most novel recent development in this field is the unique fluidless moving-bomb calorimeter described by Keith & Mackle (146). The moving-bomb has been so widely accepted because it is particularly suitable for studies of the exotic compounds already mentioned several times in this article, but it has limitations. Johnson, Prosen, and co-workers have described several well-conceived reaction calorimeters used to determine the heats of formation of compounds not easily studied by bomb calorimetry (138, 140, 217, 246). Gunn has extended the moving-bomb idea to solution calorimetry with good results (113).

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SOLUTIONS OF ELECTROLYTES IN NONAQUEOUS SOLVENTS AND MIXTURES[1]

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During recent years it has become increasingly apparent that the use of nonaqueous solvent media provides an important means of investigating ion-ion and ion-solvent interactions under extremely varied conditions. This has resulted in an ever expanding literature on both reversible and irreversible phenomena in this area. We have treated two subjects more critically than others, namely: data bearing on the testing of the recent Onsager-Fuoss conductance equation and studies relating to the nature of dilute solutions of metals. Not only are these subjects of primary interest to the authors, but they appear both to be in a state of flux and gaining in general interest, as judged by the considerable activity shown during the past year. In preparing this review we have emphasized the experimental approach. Recent theoretical developments may well await the next *Annual Review of Physical Chemistry*, particularly in view of Poirier's excellent coverage in the issue of 1959. Due to lack of space we regret omitting a number of other important subjects such as kinetics, coordination compounds, ion exchange, electrode processes, and polarography. We have only occasionally made reference to studies in aqueous solution when comparisons became profitable.

Fuoss-Onsager and Fuoss Theories of Conductance

During the past year a number of experimental papers dealing with the Fuoss-Onsager conductance theory (1) have appeared. This theory is basically an application of the interionic attraction theory to charged spheres in a solvent continuum and has been developed for unassociated, symmetrical 1–1 electrolytes. The conductance equation contains two parameters, Λ_0, the limiting conductance, and a, the distance between ions in contact, and should be capable theoretically of describing the concentration dependence of the equivalent conductance up to a concentration corresponding to $\kappa a = 0.2$, where κ is the characteristic Debye-Hückel length. An experimental demonstration of the importance of this limit has been given by Accascina, Kay & Kraus (2) for the case of Me_4N-picrate in 55 per cent dioxane-water.

Fuoss revised the original equation to make it more consistent in the re-

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tention of higher order terms. These revisions were reported in a number of publications and have been collected in one paper by Fuoss (3), in which he also includes a summary derivation of the theory without the mathematical details and an outline of the methods of analyzing conductance data for associated and unassociated electrolytes. A detailed outline of the complete theory has been published by Fuoss & Accascina (4). Graphical methods of analyzing conductance data for unassociated electrolytes and electrolytes associating into ion-pairs and higher aggregates are described, along with a recalculation of some of the earlier results of Fuoss & Onsager (1) and Fuoss & Kraus (5), which were based on the unrevised equation.

Lind, Zwolenik & Fuoss (6) have analyzed 9 sets of the most precise data for KCl in aqueous solution at 25° in order to obtain, from weighted averages, the best values for the two parameters. They conclude that their final equation can be used to calibrate conductance cells to an accuracy of 0.013 per cent.

Kay (7) has applied the equation to conductance studies of solutions of the alkali halides, nitrates, bromates, and perchlorates, in water, methanol, 50 mole per cent methanol-water, ethanol, n-propanol, and liquid ammonia at several temperatures using a weighted least-squares treatment. In water and methanol he found that the a values decreased from lithium through to cesium salts and in many cases were substantially lower than the crystallographic radii. He attributed these unreasonably low values of a to a small amount of association. This is in keeping with Fuoss' conclusion (8) that nonconducting ion pairs exist to some extent in all solvents, however high the dielectric constant, as an inevitable consequence of a model in which ions are assigned a non-zero size. For any one halide, the degree of association was postulated to increase from lithium through to cesium, an association pattern that was followed by the alkali halides in all the other nonaqueous solvents considered. Also, he showed that the ion-size parameter was completely independent of temperature between 5 and 55°, thus substantiating the earlier findings of Fuoss & Onsager (1).

Two further methods have been devised by Fuoss to obtain an ion-size parameter from conductance data. The first of these involves the use of an expression for the association constant ($K_A = 2.52 \times 10^{-27} a^3 e^b$ where $b = e^2 /aDkT$) developed by Fuoss (9) and recently reviewed by Poirier (10). This expression was derived from a sphere in a solvent continuum model and consequently excludes any contribution to K_A from solvent-solute interaction. For the sake of brevity the a obtained from the slope of a log K_A vs $1/D$ plot will be called $a(K_A)$, while that obtained directly from the Fuoss-Onsager conductance equation will be designated $a(J)$.

The third method of obtaining an ion-size parameter from conductance data comes from the dependence of the Walden product, $\Lambda_0 \eta_0$, on dielectric constant [Fuoss (11)]. Fuoss noticed that $\Lambda_0 \eta_0$ always decreased with decreasing dielectric constant, whereas no correlation could be found relating the values of $\Lambda_0 \eta_0$ with the viscosity of the solvent mixtures. This led him to consider the effect of the electrostatic forces on the hydrodynamics of the

system. It was reasoned that, due to the finite relaxation time of the solvent dipoles, a moving ion would have too few solvent dipoles oriented towards the ion in the direction of its motion, while behind, too many dipoles would still be pointing in its general direction. In effect this states that, because of the ion motion and the finite relaxation time of the solvent dipole, an asymmetry is set up in the solvent-dipole atmosphere and work must be done to move the ion against the resulting net electrostatic force. Neglecting higher order terms, he obtained the semi-empirical expression, $R^{\pm} = R_{\infty}^{\pm} + B/D$, where D is the dielectric constant and B is an unknown constant for any one ion in any one system of solvent mixtures. $R^{\pm}$ is the classical Stokes radius and is therefore proportional to $1/\lambda_0^{\pm}\eta_0$. $R_{\infty}^{\pm}$ is the hydrodynamic radius of the ion in a hypothetical solvent of infinite dielectric constant where all the electrostatic forces vanish. Since ion conductances are not available for solvent mixtures, $R^{\pm}$ was calculated by assuming the transference number in the solvent mixtures to be constant, and equal to the transference number of the ion under consideration in one of the pure solvents, generally the more polar of the two. Plots of $R^{\pm}D$ vs. D are given for the following systems: Bu_4NBr in methanol-CCl_4, ethanol-CCl_4, nitrobenzene-CCl_4, methanol-nitrobenzene, and water-dioxane mixtures; Bu_4NBPh_4 in nitrobenzene-CCl_4 and acetonitrile-CCl_4 mixtures; I^-, NO_3^-, and picrate ion in nitrobenzene-CCl_4 mixtures; Et_4N-picrate in methanol-water mixtures. In the case of solvent mixtures containing a polar and non-polar solvent, straight lines were obtained, whereas solvent mixtures containing two polar solvents yielded curves. The constant B was found to be an increasing linear function of $R_{\infty}^{\pm}$ if the solvent mixtures contained a hydrogen bonding component, whereas B was approximately a hyperbolic function of $R_{\infty}^{\pm}$ in the cases of aprotic solvent mixtures. A value for the ion-size parameter, $a(R)$, was obtained by setting $a(R) = R_{\infty}^+ + R_{\infty}^-$.

Since data were available for Bu_4NBr in three quite different systems, the ion-size parameters obtained from these methods could be compared (11). The values obtained for $a(J)$, $a(K_A)$, and $a(R)$, respectively, were 5.7 to 6.0, 5.45, 5.75 A for methanol-CCl_4 mixtures; 6.1 to 6.6, 5.45, 4.90 A for nitrobenzene-CCl_4 mixtures; 5.0 to 5.4, 4.94, 5.5 A for dioxane-water mixtures. Fuoss (11) suggested that the close agreement among all these values indicates that the ion-size parameter a can be considered as a physical constant characteristic of a given solute and independent of the solvent. Also, it was pointed out that it is impossible to separate the term in the conductance equation containing K_A from the term containing a when the association constant is small at high dielectric constants, or large at extremely low dielectric constants. Consequently, Fuoss has suggested that $a(R)$ values be used for a in the conductance equation, thereby enabling the terms to be separated and an unambiguous association constant to be calculated.

Sadek & Fuoss (12) have recalculated their earlier conductance data on Bu_4NBr in methanol-CCl_4, ethanol-CCl_4, nitrobenzene-CCl_4, and nitrobenzene-methanol mixtures. In most cases the data were not of high enough

precision to obtain $a(J)$ directly from the concentration dependence of the conductance, and a value of 6.0 A had to be assumed in order to obtain association constants. The three solvent systems containing CCl_4 gave straight lines of equal slope for log K_A vs. $1/D$ plots, indicating identical $a(K_A)$ values for Bu_4NBr in the three solvent mixtures. However, K_A was different in each solvent mixture in direct conflict with the derivation of Fuoss (9). Fuoss suggests the inclusion of a specific solvent-ion interaction term of the form developed by Gilkerson (13) to account for the differences in K_A. The nitrobenzene-methanol mixtures form an interesting system since Bu_4NBr appears to be significantly associated in each of the pure solvents but unassociated in the mixtures. An excellent discussion of the relative values of the different terms in the conductance equation over a wide range of dielectric constants has been included (12).

The conductance of Me_4N-picrate in n-butanol-methanol mixtures have been reported by Accascina & Petrucci (14), and conductances of Et_4N-picrate in the same solvent mixtures have been reported by Accascina & Antonucci (15). For Me_4N-picrate the association constant increased from 13.6 in pure methanol ($D = 32$), to 55 in a mixture containing 55 per cent n-butanol ($D = 24$). The values of $a(J)$, $a(K_A)$, and $a(R)$ were 3.8 to 4.6, 4.00, and 4.53 A, respectively. The association constants for Et_4N-picrate increased from 19 in pure methanol to 68 in a mixture containing 55 per cent n-butanol. The values obtained for $a(J)$, $a(K_A)$, and $a(R)$ were 5.19, 5.29, and 5.34 A, respectively. The fact that the $R^{\pm}D$ vs. D plots were linear is in direct contrast to what was observed by Fuoss (11) for other solvent mixtures containing two polar components. The fact that the ethyl salt is more associated than the methyl salt, despite its larger size, is explained by Fuoss & Accascina (16) by a consideration of the expression, $K_A = 2.52 \times 10^{-27} a^3 e^b$.

At high dielectric constants the cubic term will predominate and K_A should be larger for the larger ion, whereas at low dielectric constants the exponential term predominates and K_A should be larger for the smaller ion. Accascina, D'Aprano & Fuoss (17) have obtained an association constant of 0.85 for Et_4N-picrate in aqueous solution from their measurements of the conductance of this salt in methanol-water mixtures. This value was obtained by an extrapolation of a log K_A vs. $1/D$ plot from the methanol-rich mixtures, where association was considerable, to pure water. The average value of $a(J)$ obtained from the methanol-rich mixtures was 5.3 A, which did not compare favorably with the smaller $a(K_A)$ value of 3.2 A. The discrepancy was rationalized in terms of a significant dipole-ion interaction term, because of the dipole in the picrate ion, in addition to the coulombic term in the exponent b. However, this explanation is unlikely, considering the excellent agreement obtained between $a(J)$ and $a(K_A)$ for this salt in n-butanol-methanol mixtures, unless there is a substantial change in the solvent-picrate ion interaction when water is replaced by n-butanol. The conductance of Bu_4NBPh_4 in acetonitrile-CCl_4 has been reported by Accascina, Petrucci & Fuoss (18). At dielectric constants 7.2 and 4.8 they detected triple ion clustering, whereas in pure acetonitrile, association into

ion pairs was' slight ($D=36$). This salt contains two very large ions when compared to the solvent molecules and should conform well to the theoretical model. The values of $a(J)$ and $a(K)$ were 9.0 A and 8.5 A (18), respectively, whereas $a(R)$ was 7.1 A (11). Accascina & Petrucci (19) have measured this same salt in acetonitrile-benzene mixtures over the range $5 \leq D \leq 36$. The association constants obtained were identical to those obtained for acetonitrile-CCl_4 mixtures (18) at the same dielectric constant.

Accascina & Petrucci (20) and Accascina (21) have measured the conductance and viscosity of glycerol-water solutions of KCl at 25° in order to test the continuum model hydrodynamically. Measurements were carried out from pure glycerol to pure water. Although the viscosity changed a thousand-fold, the dielectric constant decreased only by a factor of 2 and remained in the range where association was not appreciable. They found that the Fuoss-Onsager equation fitted the data with $a(J) = 3.8$ A, assuming no association, indicating that the use of the macroscopic solvent viscosity in the theory is justified. However, the Walden product increased with decreasing dielectric constant in contrast to what had been found for all other systems studied.

Bock (22) has measured conductances of KIO_3 in dioxane-water mixtures down to a dielectric constant of 30 (57 per cent dioxane). In the mixtures at lower dielectric constant, association was large enough for an evaluation of $a(J)$, the values of which decreased from 3.6 to 2.0 A with increasing dielectric constant and were low when compared to the crystallographic radius of 3.53 A. The low value of 2.8 A obtained for $a(K_A)$ was attributed to dipole-ion interaction due to the dipole in the iodate ion. Fuoss & Kraus (5) used the same explanation for $NaBrO_3$ in dioxane-water mixtures.

This completes the review of papers in which the Fuoss-Onsager and Fuoss theories were discussed or applied. Since most of the discussion above involves ion-size parameters, a review paper on ionic size by Stern & Amis (23) should be mentioned. The various methods that were used to measure and calculate ion-size parameters before the Fuoss-Onsager conductance theory emerged are described and the results compared. A wide range of topics relating to the properties of solutions of electrolytes is covered in a book edited by Hamer (24). A review article by Prue (25) covers acid-base equilibria and ion association over the last few years.

CONDUCTANCE IN OTHER SALT-SOLVENT SYSTEMS

Gutmann & Baaz (26 to 29) have commenced an extensive study of the chemical and physical properties of solutions of electrolytes in phosphorus oxychloride. Solvent was obtained having a specific conductance of 2×10^{-8} ohm^{-1}cm.$^{-1}$. The conductance of a number of tetraalkylammonia salts was studied. Since the dielectric constant is 13, ion association is extensive. The data were analyzed by the method of Fuoss (30) with the following results: Λ_0 values for the salts Et_4NCl, Pr_4NCl, Bu_4NCl, Et_4NBr, and Et_4NClO_4 were respectively: 53.0, 46.3, 43.0, 49.0, and 53.4. Values of the ion-pair dissociation constant, $K \times 10^4$, were: 7.14, 13.0, 21.2, 18.9, and 6.07, respec-

tively. A linear relation was found between log K and $1/\Lambda_0$. Triethylamine also dissolves in phosphorus oxychloride to yield a conducting solution [Baaz & Gutmann (28)]. In this case $\Lambda_0 = 48.5$ and $K = 2.6 \times 10^{-6}$. A reaction of amine with solvent is postulated, followed by ionization in the sense of the equation: $Et_3N \cdot POCl_3 = Et_3NPOCl_2^+ + Cl^-$. Baaz & Gutmann (29) show further that antimony pentachloride may likewise be dissolved, forming a conducting solution with $K = 4 \times 10^{-6}$. However, the conductance changes with time, which was explained by a number of competing equilibria including the polymerization of antimony pentachloride.

Jander & Swart (31) have examined fused antimony trichloride as an ionizing solvent. The authors present an extensive survey of the literature and have determined the conductance of a wide variety of substances. The lowest value obtained for the specific conductance of solvent was $0.67 ohm^{-1}$ cm.$^{-1}$, and the value increased on standing. The high solvent conductance is attributed to the dissociation: $(x+1)SbCl_3 = SbCl_2^+ + Cl \cdot xSbCl_3^-$. The molar conductance at 99° was determined for the following chlorides (base analogues) over the concentration range 0.004 to 1.0 M: Me_4NCl, KCl, NH_4Cl, Ph_3CCl, $PhNH_3Cl$, and TlCl. The conductivities increase with dilution and approach limiting values which decrease in the order given above; in concentrated solutions TlCl is the best conductor. The following acids were also studied: $TiCl_4$, $SbCl_5$ (at 80°), $Sb(CH_3COO)_3$, $FeCl_3$, $AlCl_3$, $SeCl_4$ (at 80°), and $SbCl_2ClO_4$. The last three acids are much the poorer conductors and appear to approach limiting values that decrease in the order given above. Data are also recorded for SbOCl at 100°; solutions of $SbBr_3$ and SbI_3 did not conduct.

According to Jander & Winkler (32) the following salts, and acid or base analogues, are essentially completely dissociated in molten acetamide at 94°: Et_4NI, KI, Na-picrate, $HClO_4$, HNO_3, HBr, HCl, picric acid, p-toluolsulfonic acid, K-acetamide, Na-acetamid, Na-benzoate, Na-salicylate, Na-(o-nitrobenzoate), Na-(2,4-dinitrobenzoate), and piperidine hydrobromide. Limiting conductance values were estimated using the Onsager equation in the form suggested by Shedlovsky (33). The values ranged between 38.79 (K-acetamide) and 23.73 (p-toluolsulfonic acid). The thermodynamic dissociation constants of the weak acids 2,4-dinitrobenzoic acid, o-nitrobenzoic acid, and benzoic acid, as well as that for piperidine, were calculated from conductance measurements using the Shedlovsky (34) method. The values obtained were: 11.9, 1.18, 1.91, 2.17×10^{-3}, and 5.79×10^{-3}, respectively. The pK values in acetamide are uniformly larger than those in water, attesting to the greater basic strength of the former. The specific conductance of the solvent ranged between 2.6 and 3.5×10^{-6} ohm^{-1} cm.$^{-1}$.

The compound, $PCl_2(CF_3)_3$, is a conductor in acetonitrile [Eméleus & Harris (35)]. The solutions, however, do not conduct immediately but acquire a steady high value after standing 48 hr. The molar conductances then plot very nearly linearly against the square root of concentration to yield an extrapolated value of $\Lambda_0 = 66$. The mode of ionization was not determined

directly, but it is suggested to be of the form $P(CF_3)_3Cl_2 = P(CF_3)_3Cl^+ + P(CF_3)_3Cl_3^-$. In many respects the behavior of this system parallels that for the iodine halides [Popov & Deskin (36)] and the halogen acids in acetonitrile [Janz & Danyluk (90, 91, 92)]. In contrast, $PCl_3(CF_3)_2$ is essentially a non-conductor.

The equivalent conductance of potassium and sodium iodides, perchlorates, and thiocyanates in N,N'-dimethylbutyramide at 25° has been reported by Smiley & Sears (37). Sodium thiocyanate showed signs of being slightly associated; the other salts conformed to the Onsager square root law. These results parallel those reported for dimethylformamide [Dawson, Wilhoit & Sears (38)] and propionamide [Wilhoit & Sears (39)], but the solutions become less conducting as the molecular weight and vicosity of the solvent increase.

Goulden, Lee & Miller (40) have determined the conductance of dinitrogen tetroxide and the transport number for the NO^+ ion in 100 per cent nitric acid solution. The specific conductance compares favorably with that for solutions of potassium or ammonium nitrate. It is therefore concluded that ionization is virtually complete in the sense of the equation: $N_2O_4 = NO^+ + NO_3^-$. Transport numbers for the NO^+ ion, calculated on the premise that the anode process is $NO_2 = NO_2^+ + e^-$, lead to values slightly smaller than for the alkali metal ions [Goulden, Lee & Miller (41)]. Further evidence for complete dissociation lies in the fact that added ammonium nitrate does not appear to repress the ionization of N_2O_4.

Strohmeier & Seifert (42) have determined the conductances of the diethyl- and diphenyl-compounds of the Group II elements in the solvents benzene, ether, tetrahydrofurane, and triethylamine as a function of concentration. In all solvents the conductance increased in the order, $MgR_2 > BeR_2 > ZnR_2 > CdR_2 > HgR_2$, illustrating the dependence on the electron acceptor power of the metal. The conductance is also a function of the dielectric constant of the solvent and is further dependent upon the electron donor power of the solvent. Thus the conductances increased uniformly with increasing D in the following solvents in the order given, while the electron donating power is in the order, benzene < dioxane < triethylamine > diethyl ether < tetrahydrofurane. Hill et al. (43) have determined the conductance of sodium triphenylmethide in ether. Sodium derivatives of certain ketenes and other compounds bearing active hydrogens were nonconducting.

An interesting new solvent for use in electrochemical investigation is tetramethylene sulfone (sulfolane) which has been introduced by Burwell & Langford (44). Physical constants of the solvent, relevant to conductance measurements at 30°, are: D, 44; d, 1.2615 gm./cc.; η, 0.097 poise; solvent conductance, 2×10^{-8} ohm^{-1} cm.$^{-1}$. The conductance of tetraphenylarsonium chloride proved unique in that the conductivity appeared independent of concentration in the range between 5×10^{-3} and $1.25 \times 10^{-2} M$; this result merits further study. Negative deviations from the Onsager slope were exhibited by sodium thiocyanate, dimethylmorpholium iodide, and lithium nitrate. The Davies (45) treatment afforded ion-pair dissociation constants

of 0.021, 0.013, and 0.0011, respectively. Phenyltrimethylammonium iodide, on the other hand, appeared to be completely dissociated. Limiting conductances ranged around a value of 12.

Brewster, Schmidt & Schaap (46) have examined ethanolamine as a solvent and have accounted for the anomolous results reported by Briscoe & Dirkse (47) as being due to solvent conductance. Unfortunately it was not possible to reduce solvent conductance below $10^{-5}\text{ohm}^{-1}\text{cm.}^{-1}$; therefore it became impossible to carry out studies of high precision. In other respects the medium is ideal for electrochemical studies ($D = 37.7$, $\eta = 0.19346$ poise). Studies were made at 25° on thirteen alkali metal chlorides, bromides, iodides, nitrates, and thiocyanates, as well as silver nitrate and Bu$_4$NI. Since the data could not be treated using the Fuoss-Onsager equation (1), they were analyzed by the Shedlovsky method (34). The order of cation conductances was $K^+ > Na^+ > Ag^+ > Li^+ > Bu_4N^+$. Ion association constants for AgNO$_3$ and Bu$_4$NI were virtually the same, $1/K$ being 6.5 and 6.6, respectively. The sodium salts have uniformly lower association constants than the potassium salts and, in the case of the alkali chlorides, the order of $1/K$ is Li < Na < K. The order of anion conductances is $NO_2^- > NO_3^- > CNS^- > Cl^- > Br^- > I^-$. This order is exactly the reverse of that reported for the solvents dimethylformamide [Dawson, Wilhoit & Sears (48)] and N-methylacetamide [French & Glover (49)].

The conductances of HCl, KOH, KF, and KCl at 5 and 25° have been determined in ethanol-water mixtures by Erdey-Grúz, Kugler & Hidvégi (50, 51). The conductivities of both HCl and KOH passed through a minimum in solutions containing approximately six mole per cent water; on the other hand, the conductances of solutions of KF and KCl proved practically independent of the water content up to approximately 50 mole per cent water but they rose on increasing the water content further. A minimum appeared in the curve for HCl in a solution containing approximately four mole per cent water. For the remaining substances the viscosity-conductance product was independent of temperature below approximately 30 mole per cent water. The results are discussed in terms of ion-solvent interactions and solvation. The effect of solvent composition on the transport numbers and ionic mobilities has also been examined [Erdey-Grúz & Majthényi (52, 53)]. Similar studies have been carried out using mixtures of glycol and water [Erdey-Grúz, Kugler & Hidvégi (54); Erdey-Grúz & Majthényi (55)]. Kortolenko et al. (56) have studied the apparent molar volume, viscosity, and conductance of LiCl as a function of temperature and salt concentration in the following solvents: ethanol, 52.7 weight per cent methanol in ethanol, 47.3 weight per cent ethanol in butanol propanol, and butanol, and 82.2 weight per cent methanol in butanol.

The conductance of the 2–2 electrolyte, magnesium sulfate, in dioxane-water mixtures at 35° has been reported by Das, Das & Patnaik (57). The methods of Fuoss (30) and of Shedlovsky (34) were applied for the calculation of Λ_0 and the ion-pair dissociation constant. The values obtained by the two methods were in good agreement. Mixtures containing 0, 10, 20, and 30

weight per cent dioxane were studied. Values of Λ_0 for water and for the mixtures were: 140.84; 113.60, 95.24, and 64.10, respectively; values of $K \times 10^3$ were: 13.00, 6.56, 4.02, and 3.00, respectively, as determined by the Shedlovsky (34) treatment.

Popov & Humphrey (58) have measured the conductance of tetraphenylarsonium chloride in water, acetonitrile, ethylene dichloride, and in 70 weight per cent dioxane- and 95 per cent dioxane-water mixtures. Ion-pair dissociation constants in the last three solvents were found to be 1.12×10^{-2}, 4.81×10^{-3} and 2.3×10^{-8}, respectively; dissociation was virtually complete in water and acetonitrile. An attempt was made without success to correlate ion-pair formation with changes in the position and intensity of the ultraviolet absorption bands in the different solvents. Gutmann & Utvary (59) report the conductance of several alkylammonium salts in benzoyl bromide at 25°; solvent conductance was 6×10^{-8} ohm^{-1} cm.$^{-1}$. Limiting conductances for Pr_4NBr, Bu_4NBr, and $C_{16}H_{33}Me_3NBr$ were, respectively, 34.51, 30.47, and 33.92. Dissociation constants obtained by the method of Fuoss (30) were: 4.78×10^{-3}, 3.85×10^{-3}, and 1.81×10^{-3}, respectively. The conductance both of $TiCl_4$ and of its solutions in benzene and a number of alkyl chlorides has been measured by Longworth & Plesch (60). Conductivity is ascribed to self-ionization according to the equation: $2TiCl_4 = TiCl_3^+ + TiCl_5^-$. The authors reinterpret the results of Jacober & Kraus (61) on the conductance of $AlBr_3$ and $MeAlBr_2$ in alkyl bromides on the basis of self-ionization of the solute.

The following studies should also be mentioned. Sukhotin & Timofeeva (62) have measured the conductance of sodium iodide at 25° in mixtures of carbon tetrachloride and ethyl alcohol containing from 2.8 per cent alcohol ($D = 2.32$) to 40 per cent alcohol ($D = 13.0$), as well as in pure alcohol. Water-dioxane mixtures containing 82 per cent dioxane and 88.8 per cent dioxane were also studied. Moeller & Cullen (63) have examined the conductances of lanthanum nitrate in ethylenediamine and in ethylenediamine containing small amounts of added water. Generalized weak electrolytic behavior is indicated.

ACIDS, BASES, AND RELATED SUBJECTS

Many investigations in nonaqueous media are concerned primarily with the solvent system concept and a description of acid and base analogues. Although these studies deal largely with solutions of electrolytes, the leanings are chemical and are not intended to be precise studies of electrochemical behavior. The reader is directed to the work of Gutmann & Baaz (26 to 29) on phosphorus oxychloride, Jander & Swart (31) on fused antimony trichloride, Jander & Winkler (32, 64) on molten acetamide, and Jander & Fischer on diethylzinc (65). Reviews by Gillespie (66) and Gillespie & Robinson (67) describe the sulfuric acid solvent system. Gillespie & Oubridge (68) have carried out cryoscopic measurements on solutions of phenols in sulfuric acid and discuss solvolytic reactions. The viscosity and specific conductance of H_2SO_4–HNO_3 mixtures have been measured in the tempera-

ture range 13–50° by Surnarski & Piotrowski (69), and the results have been interpreted in terms of possible solvolytic reactions of HNO_3. Only a very limited amount of this material will be reviewed here.

Jander & Winkler (64) have carried out emf. measurements and potentiometric titrations in molten acetamide. The usual reference electrodes could not be used. Instead a special type of molybdenum electrode ("gebremste electrode"), which behaved like a hydrogen electrode, was employed. An estimate of the ion product of the solvent at 94° gave a value of 3.2×10^{-11}. A linear relation was found to hold between the emf. and -log a_H+ for HCl, HBr and other acids.

Schwabe & Schwenke (70) have studied cells of the type Pt/H_2 (1 atm.) /HCl (m), dioxane (X), H_2O $(100-X)/Hg_2Cl_2(s)/Hg$. Emf. measurements as a function of HCl molality, m, were obtained for dioxane-H_2O mixtures where $X = 20$, 45, 70, and 82 weight per cent dioxane. Standard potentials were evaluated by extrapolation to zero ionic strength; the incomplete dissociation of HCl was taken into account in solutions containing 70 and 80 per cent dioxane. By using these values the primary, secondary, and total medium effects were calculated, together with the activity coefficients for the HCl solutions. Comparison with results for a cell using a AgCl/Ag electrode give differences that have been observed previously in solutions containing methanol [Schwabe & Zeigenbalg (71)]. Similar measurements have been carried out in glycol-water mixtures by Schwabe & Hertzsch (72) using the following cell:

$$Pt/H_2 \ (1 \ atm.)/HCl(m), \quad glycol \ (X), \quad H_2O(1 - X)/Hg_2Cl_2/Hg$$

where $X = 19.25$, 50.00, and 77.91 weight per cent glycol. Activity coefficient values obtained with this cell agreed well with those obtained using a AgCl/Ag reference electrode.

Kozlenko (73) has investigated the use of the glass electrode to obtain the activity coefficients of HCl in the basic solvents quinoline and pyridine. The emf. of the following cells were determined as a function of HCl concentration.

$$Ag/AgCl/HCl(m) \ in \ quinoline/(glass)/HCl \ (0.1 \ N \ in \ H_2O)/AgCl/Ag$$

$$Hg/Hg_2Cl_2/KCl \ (sat'd. \ in \ H_2O)/HCl(m) \ in \ pyridine/(glass)/HCl \ (0.1 \ N \ in \ H_2O)/AgCl/Ag.$$
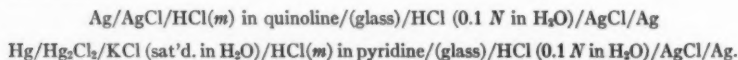
The emf. values of the first cell, together with the normal electrode potentials, permitted the calculation of the concentration dependence of the activity of HCl in quinoline. A plot of the log of the mean activity coefficient versus the square root of concentration gave a slope which agreed with theory in the limit. On the basis of known dissociation constants for HCl in pyridine, the activities of the hydrogen ion were calculated. A linear relation was found on plotting the emf. of the second cell versus -log a_H. The slope of the line was approximately 59 mv. It was concluded from these results that a hydrogen function existed for the glass electrode in these solvents.

Römberg & Cruse (74) have made an exhaustive study of the dissocia-

tion behavior of acids and bases in acetonitrile at 25°. Exact potentiometric measurements from acidimetric titrations with a glass electrode, combined with conductivity data from the literature, permitted the calculation of pK values for the following acids, given in order of decreasing strength: picric, 6.52; 3,5-dinitrobenzoic, 8.97; o-chlorobenzoic, 11.09; chloracetic, 9.81; benzoic, 11.95; acetic and trichloracetic were too weak for quantitative treatment. Values of pK_B were obtained for the following bases: piperidine, 6.88; diphenylguanidine, 6.82; triethylamine, 6.63; diethylamine, 6.60; quinoline, 12.17; pyridine and analine were too weak for quantitative treatment. The protolytic constant for acetonitrile is given as $10^{-19.45}$. Association constants for the acids are also recorded. The strengths of acids in acetophenone and benzophenone have been studied by Dulova & Popova (75). Values of pK are recorded for fourteen organic acids in acetophenone at 25°; values for four acids are given in benzophenone at 53°. Dulova & Kim (76) have also measured the strengths of acids in cyclohexanone, and Dulova, Leont'ev & Kim (77) report similar measurements for acids in cyclohexanol. Carboxylic acids are weaker by a factor of 10^{-5} and phenols, by a factor of 10^{-3}, as compared with solutions in water. Thus cyclohexanol exerts a differentiating effect on acid strengths.

The ionization of various substituted triphenylmethyl alcohols and ethers in anhydrous formic acid has been followed spectroscopically (360 to 480 mμ) at 20° by Arthur, Evans & Whittle (78). The results are discussed on the basis of the equilibrium $ROH + HCO_2H = R^+ + HCO_2^- + H_2O$ proposed by Hammett (79). The authors make use of the extinction coefficient of the carbonium ion in H_2SO_4 to calculate the carbonium ion concentration in formic acid since the spectra in the two solvents are very similar. Ionization of the alcohols appears essentially complete in all cases; ionization of the ethers studied ranges from 84 to 90 per cent.

The dissociation of valine, as well as its nickel complex, has been studied in methanol-water mixtures at 25° (80), and in dioxane-water mixtures (81) by Pelletier. Measurements of pH were made with a glass electrode. Dippy, Hughes & Rozanski (82) have determined conductimetrically the dissociation constants of a number of substituted acetic and propionic acids in acetone-water mixtures; the values are discussed in terms of chemical constitution. Yasuda (83) discusses the apparent differences in ionization constants for a particular acid in mixtures of water and organic solvents. The acids considered are succinic, adipic, benzoic, azaloic, and acetic, in water mixed with dioxane, ethanol, and methanol. The Hammett acidity function H_0 has been measured for solutions of HF and H_2SO_4 in CF_3COOH, over the entire range of concentrations by Hyman & Garber (84). Wassermann (85) has shown that a linear logarithmic relationship exists between the molar conductance and the concentration of ion-pairs formed in benzene solution from conjugate polyenes and proton donors. An estimate of the dissociation constant K may be gotten from the equation $\log \Lambda = -\frac{1}{2} \log C + \frac{1}{2} (\log K + \log \Lambda_0)$. Conductance and spectroscopic data enable an evaluation of Λ_0 and of C, the concentration of ion-pairs.

Continuing interest is being shown in the extra-mobility of the proton in water-rich media and water-like solvents. Kilpatrick (86, 87) discusses proton and hydroxyl ion mobility in water-hydrogenperoxide and water-methanol mixtures. Abnormalities in mobility are brought out by comparing, for example, limiting values of conductance for perchloric acid and potassium perchlorate in the various solvents; the ratio, $\Lambda_0(HClO_4)/\Lambda_0(KClO_4)$, is then plotted against solvent composition. Proton mobility is reduced markedly where H_2O_2 replaces H_2O in mixtures whose dielectric constant and viscosity change very little. In the case of methanol-water mixture, a minimum occurs in the ratio $\Lambda_0 (HCl)/\Lambda_0(KCl)$ at approximately 90 weight per cent methanol. Evidently the proton possesses an extra mobility in methanol as in water. In the case of KOH, the ratio $\Lambda_0(KOH)/\Lambda_0 (KCl)$ shows a minimum at 25 weight per cent H_2O_2. In pure water the ratio is 1.96; in 99 per cent H_2O_2 it is 1.83. The author suggests that the abnormal conductance of the OH^- ion is destroyed but that more mobile hydroperoxide ions are produced, thus accounting for the minimum. In methanol-water mixtures there is no minimum, but a continued decrease occurs with added methanol. The conductance of the proton apparently is not abnormal in anhydrous HF, but the fluoride ion has an unusually high mobility. The conductivity of HCl in H_2O-propan-1-ol and -propan-2-ol mixtures and its relation to abnormal proton mobility have been investigated by Tourky & Mikhail (88). The investigations of Erdey-Grúz *et al.* (50 to 55) on the conductance of HCl and KOH in ethanol-water and glycol-water systems have already been mentioned.

The properties of HCl dissolved in acetone have been examined by Dorofeeva & Kudva (89). Tables and graphs are given for density, specific conductance, and molar conductance. The molar conductance passes through a maximum at $1.32 M$ and a minimum at $0.087 M$. Janz & Danyluk (90, 91, 92) have made a thorough study of the conductivities of HCl, HBr, and HI in acetonitrile at 25°. In these systems the conductance increases with time. Possible ionization processes, which will account for this behavior, are considered, and the nature of the solid substrates, e.g., $CH_3CN \cdot 2HCl$, is discussed. It was not found possible to account for the form of the conductance-concentration curves using existing methods of treating data for weak electrolytes. Proton resonance shifts have been studied for the systems, $HNO_3 - H_2O$ and $HNO_3 - KNO_3$, by Happe & Whittaker (93). A nuclear magnetic resonance study of the protolysis kinetics in methanol, ethanol, and in mixtures with water is reported by Luz, Gill & Meiboom (94).

SOLUTIONS OF METALS

Certain metals, notably the alkali metals, dissolve in liquid ammonia and other solvents to yield electrically conducting solutions. Dilute solutions, below approximately 0.01 N, resemble solutions of normal electrolytes in many respects, and the discussion will be restricted to these. There is almost universal agreement that, on dissolving, the metal undergoes complete dissociation in the sense of the equation $Metal = M^+ + e^-$ where M^+ is the

metal ion and e^- is the electron. What occurs mechanistically to determine the state of the system, after the primary dissociation, is subject to debate.

There are two principal schools of thought, both of which were proposed initially to explain the properties of solutions of metals in liquid ammonia. One model, the cavitation model, was first suggested substantially in its present form by Ogg (95) and subsequently championed by Hill (96), Lipscomb (97), Kaplan & Kittle (98), and others. In this model the "solvated" electron is presumed to reside in a spherical cavity of volume equivalent to approximately one solvent molecule. Increasing the concentration or lowering the temperature favors electron pairing in the cavity. Thus we have the equilibrium $2e^- = e_2^=$, which, to a first approximation, is considered independent of the nature of the metal ion. The second model, the mass action or expanded metal model, as proposed by Becker, Lindquist & Alder (99), formulates the problem somewhat differently. Four species are considered: (a) a solvated metal ion, M^+; (b) a solvated electron, e^-; (c) a monomer or expanded metal atom, M, consisting of a solvated metal ion with an electron circulating among the hydrogen atoms of the solvating ammonia molecules, and; (d) a diamagnetic dimer M_2 consisting of two monomers held together chiefly by exchange forces. The species form a system in dynamic equilibrium which may be characterized by two equilibrium constants, namely,

$$M = M^+ + e^- \qquad K_1 = [M^+][e^-]/[M] \qquad\qquad 1.$$

$$M = 1/2 M_2 \qquad K_2 = [M_2]^{1/2}/[M] \qquad\qquad 2.$$

One essential feature of this model, as it differs from the cavitation model, is the inclusion of the metal ion as an important entity in determining the state of the system.

Both theories account fairly satisfactorily for the effect of metal concentration and temperature on the magnetic properties. Upon using the data of Hutchison & Pastor (100) on the paramagnetic resonance of solutions of potassium, Kaplan & Kittle (98) obtained a reasonably good reproduction of the static field results of Freed & Sugarman (101) based on the cavitation model. Even better agreement with experiment was obtained by Becker et al. (99) using the mass action model; in addition, it became possible to justify differences in the susceptibilities of solutions of potassium and sodium.

While magnetic data have been of prime importance in developing models for metal solutions, in that they unequivocally establish the presence of both para- and diamagnetic species, an acceptable model must also account satisfactorily for other properties, as electrical conductivity and electronic spectra. The mass action model appears particularly well suited to describing the concentration dependence of the conductance of dilute metal solutions. This result is of prime importance since conductance data are the only precise data available at high dilutions showing the concentration dependence of the phenomenon under observation. Evers & Frank (102) have assumed that the conducting species follow the laws governing the be-

havior of dilute solutions of electrolytes and have derived what is essentially the Shedlovsky equation (34) for ion-pairing, corrected for the presence of dimers. An analysis of the early data of Kraus (103) on solutions of sodium in ammonia provided the following constants: $\Lambda_0 = 1022$, $K_1 = 7.23 \times 10^{-3}$, and $K_2 = 27.0$. The equation reproduced the experimental data to concentrations as high as approximately 0.04 N. The analysis has recently been extended to data on solutions of lithium in methylamine at $-78°$ with equally good success [Berns, Evers & Frank (104)]. The constants obtained were: $\Lambda_0 = 228.3$, $K_1 = 5.79 \times 10^{-6}$, and $K_2 = 5.42$. It may be noted that the values for the constants for monomer dissociation are in the range of those found for normal salts [Filbert (105)].

Like magnetic measurements, conductivity data do not provide us with a detailed knowledge of the structure of the components of the systems. They only furnish us with some indication of the limiting mobilities and the numbers of conducting particles, assuming that the mass action hypothesis is valid. However, direct evidence for the existence of metal ion-electron interaction is demonstrated by the nuclear magnetic resonance studies of McConnell & Holm (106). An appreciable Knight shift (107) was observed for the Na nucleus in solutions of sodium in ammonia, which means there must exist at least one kind of electron trap associated in some way with the metal ion. Using the Becker model, Blumberg & Das (108) were able to calculate the experimentally observed dependence of the Knight shift for the Na and N nuclei simultaneously; the fact that no shift was observed for H was also accounted for in their calculations. The treatment of the problem follows formally the one found successful in treating the hyperfine interaction of F centers [Blumberg & Das (109)]. It was not found necessary to invoke the existence of definite e^- species in the bulk solvent to explain the experimental results; but this does not preclude their existence, as the authors point out. Unfortunately, the experimental data do not go below approximately 0.1 N. Obviously, with the mass action model, e^- traps and M^+ ions become increasingly more important species relative to M and M_2 as the concentration is decreased. However, the nuclear magnetic resonance data definitely indicate the existence of monomer units.

The electronic spectra of metal solutions have been examined in a variety of solvents and solvent mixtures and over considerable ranges of temperature. Measurements have been largely limited to very dilute solutions of the order of $1 \times 10^{-3} N$ or less. Two bands are found; one or both are present depending on temperature, concentration, the nature of the solvent media, and, to some extent, on the metal itself. One band maximum is found in the visible region at $\sim 15,000$ cm.$^{-1}$ and one in the infrared at $\sim 7,000$ cm.$^{-1}$. For example, very dilute solutions in ammonia show only the infrared band [Blades & Hodgins (110)]; thin films of more concentrated solutions show both bands at 20°K. [Bosch (111)]. Lithium in methylamine shows both bands, whereas sodium shows only the visible band [Hohlstein & Wannagat (112, 113)]. In ethylamine (110) and certain diamines the visible band predominates [Fowles, McGregor & Symons (114)]. Solutions in the polyethers show only the visible band [Down et al. (115); Cafasso & Sundheim (116)].

Symons *et al.* (114, 117, 118) have pointed out that a close connection exists between the spectra and magnetic properties of metal solutions. Where comparative data are available it has been found that solutions exhibiting an absorption band only in the visible are diamagnetic; those possessing both bands or only the band in the infrared are paramagnetic. Lowering the temperature or increasing the metal concentration appears to favor the visible band at the expense of the infrared band. These results have led Fowles *et al.* (114) to suggest that the visible band is to be associated with the diamagnetic M_2 species while that in the infrared is due to paramagnetic species.

Symons (117, 118) concludes that in dilute solutions (in ammonia) the only paramagnetic species that has to be considered is the solvated electron. Doubtless this is correct at high dilutions, and many supporting arguments may be presented, e.g., that the magnetic curves appear to extrapolate to a value consistent with an Avogadro number of spins at infinite dilution. The limiting conductance value of 1022 for sodium in ammonia, while approximately three times the value for normal electrolytes, is not excessive [Hnizda & Kraus (119)]. An extra-mobility is indicated for the negative carrier, the electron, much like that for the proton in water, but the electron must be fairly tightly bound to the solvent. Recent theoretical studies by Jortner (120) concerning the state of the solvated electron at infinite dilution are in accord with this view. It was possible to obtain a theoretical value for the heat of solution of the electron in agreement with experiment and to show that the energy of the $1s \rightarrow 2p$ transition is in accord with the band observed in the infrared.

Symons (117, 118), however, proceeds further and primarily on the basis of magnetic and optical data suggests that the properties of dilute solutions in all solvents may be explained adequately in terms of a hybrid model in which the only two components needing serious consideration are the dimer and the trapped electron. This seems very unlikely if we adopt the pseudo-electrolytic point of view and take the results of the analysis of conductivity data seriously. For example, using the mass action constants derived from conductance data, it may be computed that at a metal concentration of $1 \times 10^{-3} N$ para- and diamagnetic species are present in the following relative abundances: for sodium in ammonia at $-34°$, $e^- = 90.3$ per cent, $M = 6.4$ per cent, and $M_2 = 3.3$ per cent; and for lithium in methylamine at $-78°$: 28.8, 69.6, and 1.6, respectively. At $1 \times 10^{-2} N$, the values are: 76.4, 12.0, 11.6; and 15.2, 71.7, and 13.1 per cent, respectively.

One difficulty seems to be in defining what is meant by a dilute solution. In the case of normal electrolytes in ammonia, a solution $1 \times 10^{-3} N$ might be thought of as being moderately dilute, i.e., there is measurable ion association to pairs; in an ether such a solution would be considered very concentrated, with association being extensive. If the analogy holds, then considerable association to monomer might be expected in a solvent like methylamine; in a solvent of low dielectric constant like 1,2–dimethoxyethane there could probably be virtually complete conversion to diamagnetic dimers or other diamagnetic species. Conductivity data seem to bear out this an-

alogy and imply that the influence of the monomer species can hardly be neglected in the concentration range considered above, although it is of considerably less importance in ammonia than in methylamine.

The presence of substantial quantities of monomer under certain conditions is not in disagreement with the magnetic and electrical properties of metal solutions as we know them, and probably not with the electronic spectra either. The question then arises as to the position of the monomer absorption band, if it exists. According to Symons (118) the monomer band should occur at roughly 12,500 cm.$^{-1}$ since the addition of large quantities of sodium salt to dilute solutions of sodium in ammonia produced a new band at about 12,500 cm.$^{-1}$ The new band was attributed to the monomer formed by repression of equilibrium (i), above [Clark, Horsfield & Symons (121)]. Solutions of potassium in methyamine show just such a band at 12,500 cm.$^{-1}$, as well as one at 15,000 cm.$^{-1}$ [Blades & Hodgins (110)]. It is reasonable to suppose that the monomer should absorb in the visible, as pointed out by Symons, and it may well overlap that of the dimer so as to become indistinguishable. In conclusion, unless the conductance data are greatly in error, which seems unlikely, and the interpretation of the results are unsound theoretically, it is probably necessary to reexamine our interpretation of the spectral data, at least insofar as the band in the visible is concerned. Quantitative data covering all aspects of the problem are needed badly.

One other recent observation seems important. Although solutions of potassium in 1,2-dimethoxyethane display no paramagnetic resonance and absorb only in the visible, therefore presumably containing only dimers, they are electrical conductors [Cafasso & Sundheim (116)]. Thus, at $-40.1°$ a solution 1.75×10^{-4} N in metal had an equivalent conductance of 15.9; also, solutions of lithium in ethylamine at $-23°$ are conductors [Young (122)]. An adequate explanation of this phenomenon awaits further experimentation.

MISCELLANY

Sukhotin & Timofeeva (123) have measured the emf. at 25° of the cell

$$\text{Na(Hg)/NaI soln./AgI/Ag}$$
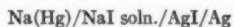
containing NaI dissolved in a CCl_4-ethanol containing mixture 90.4 percent by weight of CCl_4 ($D = 3.4$). A method is outlined for obtaining standard potentials and for computing ion activity coefficients. The mean ion activity coefficient was also obtained for HCl dissolved in an 18 per cent by weight water-dioxane mixture. Steel $et\ al.$ (124) have evaluated individual limiting ionic mobilities in aqueous solutions containing 10 weight per cent mannitol, 10 and 20 per cent sucrose, and 10 and 20 per cent glycerol. For very large ions the values approach those predicted by Walden's rule in water, but for smaller ions, and in particular for the proton, the mobility is lowered less than predicted by Walden's rule [cf. Accascina $et\ al.$ (20, 21)]. The results are discussed in terms of a model suggested by Wang (125) to account for self-diffusion of water in protein solutions. Artemchenko (126) has measured the viscosities of solutions of NaI in methanol. Unlike solutions in water, a negative viscosity coefficient is not observed.

Austin, Matheson & Parton (127) have determined the enthalpy of association for the system, $PbBr_2 = PbBr^+ + Br^-$, calorimetrically, in water and in water containing up to 61.01 mole per cent methanol. The value in the latter medium was 2070 cal. as compared with 300 cal. in pure water.

Coulter *et al.* (128) report that the standard free energy of formation at 240°K of the amide ion in liquid ammonia, in a hypothetical 1 molal solution, is -19.3 cal.deg^{-1} mole^{-1}, relative to $S_{240°K}(H_{am}^+) = 0.0$. For the self-ionization of ammonia, they give the value $K_{NH_3} = 3.2 \times 10^{-33}$ at 240°K. Values are also reported at 298.15°K. Stewart & Wendlandt (129) report the solubility and enthalpy of solution at 25° for $La(NO_3)_3 \cdot 6H_2O$ in 19 monobasic alcohols and 14 other organic solvents.

An interesting study by Inami & Ramsey (130) has provided evidence that solutions of electrolytes in ethylene dichloride enhance the mole ratio of the *gauche* to *trans* forms. By comparing infrared spectra of pure solvent with solutions containing 0.77 and 1.23 volume formality of Bu_4NClO_4, it was shown that the mole ratios are 1.69 and 1.92, respectively, which are well above the value of 1.3 for pure solvent. These results are in accord with the observation that dissociation constants for ion-pairs in ethylene dichloride ($D = 10.23$) are a factor of ten larger than those in ethylidine dichloride ($D = 9.90$) [Denison & Ramsey (131)]. This result is explained by the interaction of the *gauche* dipoles with the ions, which causes the effective dielectric constant to be larger than the macroscopic value.

A cryoscopic study of the association of some lithium salts in acetic acid has been carried out by Kenttämaa (132). Dimers were formed, predominantly by lithium halides; $LiNO_3$ apparently formed a trimer. The degree of association increases in the order: $LiCl < LiBr < LiI$. Jander & Swart (31) have obtained cryoscopic data in fused antimony trichloride covering the concentration range 0.01 to 0.03 M for the following compounds: Ph_3CCl, Me_4NCl, $PHNH_3Cl$, KCl, $TlCl$, $SbOCl$, $Sb(CH_3COO)_3$, $TeCl_4$, and $SeCl_4$. The v'ant Hoff factor, i, for the last two substances was essentially unity, increasing slightly with dilution. For antimony triacetate, on the other hand, the factor was three, indicating solvolysis, probably to $SbCl_2$ (CH_3COO). The factor for the remaining compounds was essentially two and increased with dilution.

The dipole moments in benzene of three long-chain amine sulfates and bisulfates have been measured by McDowell & Allen (133). The values are lower than those for short-chain salts reported by Geddes & Kraus (134). The heat conductivity of six 1–1 and 1–2 salts in methanol and acetone is reported by El'darov (135). Ultrasonic absorption due to chemical relaxation in solutions of electrolytes is reviewed by Verma (136). Data in the mixed solvents (water-dioxane, -methanol and -ethanol) are discussed. Winstein, Smith & Darwish (137) point out that added salts in solvents of low dielectric constant greatly accelerate the ionization of organic substrates, such as alkyl toluenesulfonates; hence the inclusion of salts may drastically alter the relative ionizing power of solvents. For example, in ether the rate of ionization of p-methoxyneophyl p-toluenesulfonate is increased by a factor of 10^5 by 0.1 M lithium perchlorate. Finally, it seems

appropriate to bring to the attention of chemists that the ion-pair equilibrium concepts of Bjerrum (138) and of Fuoss (30) have been applied successfully to the interpretation of phenomena in doped germanium and silicon. Developments along these lines have been due largely to Reiss *et al.* (139) and the results have been reviewed recently by Fuller (140).

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GASEOUS REACTIONS[1]

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Theory

Several significant theoretical and experimental advances have been made in the study of gaseous reactions during 1959. Major improvements have been made in the theories of energy transfer processes and unimolecular reactions. Many of the experimental achievements have been the direct result of highly improved analytical methods, chiefly in the areas of mass spectrometry and gas chromatography. In many cases the use of the new analytical tools in the re-examination of "thoroughly studied and completely understood" reactions has led to new and interesting details of the mechanism.

Theory of unimolecular reactions.—Recently Slater has published a book based on a series of lectures given at Cornell University; he considers the ideas and problems concerned with the theory of unimolecular reactions (1). This work will be particularly valuable since it serves to draw together Slater's ideas and those of others that have been published in widely scattered journals (some rather inaccessible) for over 30 years. Numerous tests of the different theories of unimolecular reactions have been made in the past year. Commonly the rates have been considered in light of the theories of Hinshelwood (2), Kassel (3, 4), and Rice & Ramsperger (5, 6); H.K.R.R., on the one hand, and Slater on the other (1; 7 to 13). In contrast to the H.K.R.R. assumption of free energy exchange between the various molecular modes of excitation, the Slater theory assumes no energy exchange between the normal modes. Reaction occurs not when the energy gets into a particular mode, but when the normal-mode vibrations come suitably into phase, that is, some critical co-ordinate becomes sufficiently extended. Gill & Laidler have made the most extensive of these tests of theory. They have reconsidered the published data for N_2O (14), O_3 (15), and H_2O_2 (16) from the standpoint of unimolecular reaction rate theory. In a very comprehensive work these authors also have treated the decompositions of N_2O_5, C_2H_6, *cyclo*-C_3H_6, and C_2H_5Cl (17). They conclude that for N_2O, H_2O_2, and C_2H_6 decompositions, Slater's rates of energization are too low by a significant factor, whereas the H.K.R.R. theories can give a satisfactory interpretation. The rates that they calculate according to Slater's theory for O_3, N_2O_5, *cyclo*-

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[1] The publications discussed in this review were selected from the literature that appeared between November 15, 1958 and November 15, 1959; reference to the Russian literature is restricted to those journals that were published in the year 1958 and became available in English translation during 1959.

C_3H_6, and C_2H_5Cl appear to be of the correct order of magnitude, while the H.K.R.R. rates are too high unless one employs fewer degrees of freedom than are actually present in the molecule. They conclude that the hypothesis of the Slater theory is correct as far as the mechanism of breakdown of the energized molecule is concerned, but it is not always correct with regard to the rate of energization of the molecules. Thiele & Wilson (18) also find disagreement between the experimental data for cyclo-C_4H_8, cyclo-C_4H_6, and N_2O_5 and Slater's theory; they conclude that perhaps the inclusion of fairly substantial anharmonicity interactions between normal modes and some other type of collisional activation mechanism may be necessary to improve the theory. Gill & Laidler suggest as modification of the unimolecular reaction rate theory, a compromise between the assumptions of the Slater and the H.K.R.R. theories (17). They have proposed that there is a definite probability of energy flow between normal modes of a molecule A', energized in the H.K.R.R. sense (but not having the right distribution of energy to be energized according to the Slater picture) and the Slater energized molecule, A^*. They have generalized the various activation and energy flow processes as follows (The symbolism is that of Gill & Laidler; the superscripts, H and S, designate constants associated with the H.K.R.R., and Slater theories, respectively.):

$$A + A \underset{k_{-1}^H}{\overset{k_1^H}{\rightleftharpoons}} A' + A$$

$$k_{-1}^S \diagdown \quad k_1^S \quad \diagup k_s \quad \diagdown k_{-s}$$

$$A^* + A$$

$$\downarrow k_2^S$$

Decomposition Products
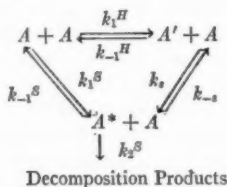
In terms of steady treatment of this reaction mechanism, the rate of reaction, v, becomes:

$$v = \frac{k_2^S[A]^2\{k_1^S k_{-1}^H[A] + k_s(k_1^S + k_1^H)\}}{k_{-1}^H(k_{-1}^S[A] + k_2^S)[A] + (k_s k_{-1}^S + k_{-s} k_{-1}^H)[A] + k_s k_2^S}$$

In the event that k_s and k_{-s} are small (no energy flow, as is assumed in the Slater picture), then $v = (k_2^S k_1^S/k_{-1}^S)[A]$. Thus Slater's expression for the high pressure rate will always apply even if k_s is large. At low pressures the expression reduces to $v = (k_1^S + k_1^H)[A]^2$. Since k_1^H is probably always greater than k_1^S this reduces to $v = k_1^H[A]^2$. Hence it is concluded that at low pressures the rate should be given by the H.K.R.R. formula for the rate of energization. Both classical and quantum mechanical reasoning are used to show that the rate constants for energy flow, k_s, k_{-s}, are expected to be greater the smaller the number of normal modes in a molecule. The quantitative evaluation of the rates of energy flow has not yet been successfully treated theoretically.

Slater (19) has recently determined that the only model for which the first-order rate constant for unimolecular decomposition is precisely of the

Arrhenius form, is a system of degenerate harmonic oscillators similar to the model of Kassel. Steel (20) has reconsidered the theory of "high" frequency factors in unimolecular reactions in terms of an extended Kassel-type model in which the critical energy is localized in more than one oscillator. Mahan (21) has derived the activation rate in unimolecular reactions using a step-wise formulation based on the multibarrier kinetic problem developed by Eyring and co-workers (22, 23). A new term involving the free energy difference between two consecutive barriers appears in the theoretical rate equation. Powell has presented another of his most useful graphical methods for treatment of kinetic data (24). A logarithmic plot of k_1 against k_2, the apparent first- and second-order rate constants, is matched against a family of theoretical curves. The procedure enables one to evaluate the high and the low pressure-limiting rate constants, and the parabolic exponent from unimolecular reaction rate data.

Other theoretical developments.—Szabó (25) suggests a simplifying modification of the usual methods used to study kinetic data from chain reactions. All reactions but one in each stage (initiation, propagation, branching, and termination) are rejected by application of kinetic principles; then the whole reaction sequence can be described by two simple differential equations, one for chain carrier, the other for concentration of initial substances. The method is used to treat experimental data from the thermal decomposition of SO_2Cl_2 (26), and ClO_2 (27).

A new general collision theory has been described by Eliason & Hirschfelder (28). It should be of special interest for the treatment of rates of bimolecular reactions involving non-adiabatic molecular encounters (reactions in shock tubes, molecular beams, etc.) where Maxwell-Boltzman energy distribution cannot be assumed. It is similar in approach to that used by Wang-Chang & Uhlenbeck (29) to calculate transport properties of polyatomic molecules. Provotorov (30) has presented a theory of chemical reactions of atoms with energies comparable to the energy of activation in which the rate constant is calculated by the activated complex method. Nikitin (31), Rice (32), and Widom (33) have developed revised collision theories for the rates of dissociation of diatomic molecules. Jepsen & Hirschfelder (34) derive an expression for the rate of recombination of atoms and the rate of reaction, $A+BC \rightarrow AB+C$, in terms of the collision dynamics of three potential well atoms restricted to move on a line. Yasumori (35) has continued his theoretical treatment of reactions in terms of potential energy surfaces. A modified bond eigen-function method of constructing the potential energy surface of a reaction is developed (36) and applied to the $H-H_2$ reaction (37). The method of Yasumori appears to give marked improvement in the theoretical estimation of the absolute energy of the H_3 complex. Nicholas (38) has extended the treatment of Rüetschi (39) to derive relations between activation energies (E) and pre-exponential factors (A) for individual rate steps and the apparent E's and A's for processes involving competing mechanisms of several types.

Sinanoglu & Pitzer (40) present a new and simplified method of deriving

theoretical pre-exponential rate factors for abstraction reactions that should be very useful to the calculation-weary kineticist. Classical partition functions are used that require only a knowledge of several force constants and bond lengths; detailed structural information on reactants and complex, and the calculation of moments of inertia and vibrational frequencies are unnecessary. The calculated pre-exponential factors (log A, cc./mole-sec.) for the H-abstraction reactions of the given pairs of reactants are as follows: CD_3—C_2H_6, 11.76; CF_3—C_2H_6, 11.17; CF_3—C_2H_8, 11.29; CF_3—nC_4H_{10}, 11.39; for the reaction, $Br + BrCCl_3 \rightarrow Br_2 + CCl_3$, 13.33. Agreement with experimental estimates of A was within a factor of 3.7 in the most divergent case. Yankwich & Ikeda (41) have derived theoretical estimates for the pre-exponential factor in the rate constant ratio for isotopic reactions involving planar four-center systems. The results are used to elucidate the mechanism of the solution phase acid-catalyzed urea decomposition, but they should also be useful in future applications to gas phase isotopic reactions presumed to involve similar four-center activated complexes.

ELEMENTARY REACTIONS OF ATOMS

Halogen atom combination reactions.—Givens & Willard (42) have restudied the Br-atom recombination reaction from 0–145°C. using the flash photolysis technique.

$$Br + Br + M \rightarrow Br_2 + M \qquad\qquad 1.$$

The apparent values of E_1 for Ar and Br_2 as M were found to be -1.4 and -2.9 kcal./mole, respectively. The data suggest that the intermolecular attractions exerted by halogen molecules on halogen atoms are not a highly specific type. Husain & Pritchard (43) have suggested a new simple theory to explain the negative energies of activation associated with halogen atom recombinations. It is based on the assumption that only those atoms in a complex that have energies within a small range of values will undergo deactivation on collision. Porter & Smith (44) feel that the variation of rate of reaction 1 (and of the analogous I_2 reactions) with different M's, the strong interactions as measured by the magnitude of $-E$ (much higher than van der Waal forces), and the various other facts related to reaction 1, are all consistent with the participation of a charge-transfer complex between the halogen atom and M.

H-atom abstraction reactions of halogen atoms.—Several extensive studies of the relative rates of H-atom abstraction have been reported

$$X + RH \rightarrow XH + R \qquad\qquad 2.$$

in the past year. Anson, Fredricks, & Tedder (45) have fluorinated, chlorinated, and brominated n-C_4H_{10} and iso-C_4H_{10} and have derived the following ratio of rate constants for H-atom abstraction per single C—H bond; the s, p, and t superscripts refer to primary, secondary, and tertiary C—H bonds, respectively: for Cl atoms, $k_2^s/k_2^p = 1.8$ exp (480 cal./RT); $k_2^t/k_2^p = 2.1$ exp (540/RT); for F atoms, $k_2^s/k_2^p \cong 1.1$ exp (97/RT), for Br atoms

(146°C.), $k_2{}^s/k_2{}^p \cong 82$. $k_2{}^t/k_2{}^p \cong 1640$. Knox & Nelson (46) have determined the relative rates of chlorination for a number of pairs of H-containing compounds (RH). The experimental ratios of the pre-exponential factors are checked against theoretical estimates of these ratios. The comparison shows that vibrational entropy of activation increases as RH becomes more complex. While the major part of this arises from the introduction of low frequency bending and wagging of the R—H—Cl part of the complex, alteration in the frequencies of the low-energy chain deformation vibrations must be involved to account for secondary effects (such as higher vibrational entropy of activation for attack at *sec.*- than at *primary*-C—H bonds). Mercer & Pritchard (47) report that the activation energy difference between reaction 2 for the reactants F—H$_2$ and F—CH$_4$ is 0.5 ± 0.2 kcal./mole.

Fettis & Trotman-Dickenson (48) have derived C—H bond dissociation energy data for simple hydrocarbons from competitive bromination rate data using the technique of Kistiakowsky & Van Artsdalen (49). Kinetic studies of the chlorination of C_2Cl_4 (50), C_2Cl_3H (50), and cyclopentanone (51) have appeared. An interesting stereospecificity in the chlorination of 2-chlorobutane has been observed by Fredricks & Tedder (52). The ratio of *meso*:*racemic*-2,3-dichlorobutane is 2.4:1 at 78°C. This may indicate preferred conformations for the intermediate radical, $CH_3CHCHClCH_3$. If so, this is the first observation of such a phenomenon in the gas phase. These authors have also reconsidered the theoretical interpretations given to explain the order of ease of H-atom abstraction by halogen atoms (53). The relative rates of chlorination of the *sec.*-H's in *n*-butane, *n*-hexane, 1-chlorobutane, 1-chloropentane, 1-fluorobutane, and 1-fluoropentane, suggest that the difference in observed reactivities does not correlate as well with polar effects as with the importance of resonance stabilization of the incipient alkyl radical by hyperconjugation.

Other halogen atom reactions.—New rate data from the photolysis of bromine in chlorine and published data for k_1 were used by Christie, Roy & Thrush (54) to derive the rate constants for the following reactions:

$$Br + Cl_2 \rightarrow BrCl + Cl \qquad\qquad 3.$$
$$Cl + BrCl \rightarrow Cl_2 + Br \qquad\qquad 4.$$
$$Cl + Br_2 \rightarrow ClBr + Br \qquad\qquad 5.$$
$$Br + BrCl \rightarrow Br_2 + Cl \qquad\qquad 6.$$
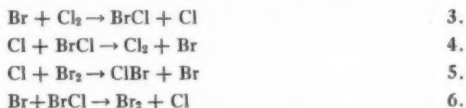
$k_3 = 4.5 \times 10^9 \exp(-6.9 \text{ kcal.}/RT)$ 1./mole-sec.; $k_4 = 2.0 \times 10^9 \exp(-1.1/RT)$; $k_5 = 2.3 \times 10^8$ at 20°C.; $k_6 = 3.4 \times 10^3$ at 20°C.; $k_1(M = Cl_2) = 3.0 \times 10^{10}$ 1.^{2}/mole^2-sec. at 20°C. The same authors derive $k_7 = 5 \times 10^8 \exp(-4.5$ kcal./$RT)$ 1./mole-sec. from rate data from the photolysis of ICl (55).

$$Cl + ICl \rightarrow Cl_2 + I \qquad\qquad 7.$$

Benson & Anderson have trapped at liquid nitrogen temperature an unknown interesting unstable product of the photolysis of Cl$_2$ in O$_2$; it may be ClO, Cl$_2$O$_2$, or ClOO (56).

Nitrogen atom reactions.—Two independent estimates of the rate of the recombination of N-atoms have been reported in the past year. Kelly & Winkler (57) monitored the N-atom concentration by measuring the rate of HCN production from C_2H_4 or C_2H_6. Both surface and homogeneous combinations occurred. The homogeneous reaction rate constant was in the range, 4.8×10^{14} (cc.^{2}/mole^2-sec.) $\leq k_8 \leq 8.5 \times 10^{14}$ at 55°C. and $2.9 \times 10^{15} \leq k_8$ $\leq 4.8 \times 10^{15}$ at 400°C.; the range of values stems from an uncertainty as to whether N-atoms and N_2 are considered equivalent or non-equivalent as M.

$$N + N + M \rightarrow N_2 + M \qquad\qquad 8.$$

Herron *et al.* (58) followed the N-atom concentration by using NO as a titrant, and they estimate $k_8 = 5.7 \times 10^{15}$cc.^{2}/mole^2-sec. (independent of the temperature in the range $-78°$ to 177°C.). The efficiencies of the different third bodies, N_2, He, and Ar as M in reaction 8 were approximately as found for the recombinations of I or Br atoms. Kelly & Winkler (57) find relatively good agreement between their estimate of k_8 and the measured rate of afterglow (59) following N-atom association; they suggest that all of the homogeneous decay of N-atoms can be explained by the Berkowitz, Chupka & Kistiakowsky mechanism (59). Studies of the reactions of N-atoms with various molecules (C_2H_2, C_2H_4, HBr, etc.) have continued (60, 61, 62). The complexity of these reactions is impressive.

Oxygen atom reactions.—The reaction of oxygen atoms with various un-saturated molecules has received considerable attention. Cvetanović (63) determined the relative rates of addition of oxygen atoms (^{3}P) to a variety of olefins at room temperature. Very systematic variations of the rates of addition are observed and correlate well with the conventional electronic theories of reactions common to physical organic chemistry. In a series of very well conceived experiments, Cvetanović, Sato & Jarvie (64, 65, 66) found that $O(^1D)$ and $O(^3P)$ atoms each react in distinctive and predictable fashions with the butenes. The $O(^1D)$ atom shows the theoretically expected higher stereospecificity in its addition to the double bond. Harteck, Reeves & Mannella (67) have redetermined the rate constant for the reaction, $NO + O + M \rightarrow NO_2 + M$; $k = 7.6 \times 10^{-32}$cc.^{2}/molecule^2-sec. at room temperature: M was mainly Ar.

ELEMENTARY REACTIONS OF FREE RADICALS

H-atom abstraction reactions of free radicals.—Klein *et al.* (68) have measured the ratio of rate constants k_9/k_{10} and k_{11}/k_{10} by photolysis of CD_2O mixtures with H_2 or CH_4 at temperatures near 350°C. Published data for the $H - H_2$ reaction (69) were used to

$$D + D_2CO \rightarrow D_2 + DCO \qquad\qquad 9.$$
$$D + H_2 \rightarrow DH + H \qquad\qquad 10.$$
$$D + CH_4 \rightarrow DH + CH_3 \qquad\qquad 11.$$

derive the following data: $E_{10} = 5.4$, $P_{10} = 0.11$; $E_9 = 4.8$, $P_9 = 0.04$; $E_{11} = 7.8$ kcal./mole, $P_{11} = 0.025$. Dainton, Ivin & Wilkinson (70) have redetermined

the rate of reaction 12 through the photolysis of $^{14}CH_4$-acetone mixtures (temperature, 200 to 350°C.).

$$CH_3 + {}^{14}CH_4 \rightarrow CH_4 + {}^{14}CH_3 \qquad\qquad 12.$$

They find $k_{12} = 10^{8.83}$ exp (-14.7 kcal./RT) 1./mole-sec. The rate of the possible group displacement reaction 13 is at most about 3.6 per cent of the rate of 12 at 350°C.

$$^{14}CH_3 + CH_3COCH_3 \rightarrow CH_3 + {}^{14}CH_3COCH_3 \qquad\qquad 13.$$
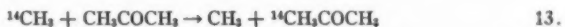
Summarized in Table I are recent rate data for several H-atom abstraction reactions measured relative to the radical combination rate. Some rather interesting and unexpected variations are found in the comparison

TABLE I

H-Atom Abstraction Reactions of Alkyl Radicals

$$R + R'H \rightarrow RH + R' \qquad\qquad a.$$
$$2R \rightarrow R_2 \qquad\qquad\qquad b.$$

R	R'H	$E_a - E_b/2$, kcal./mole	log $(A_a/A_b^{1/2})$ (A, cc./mole-sec.)	Investigators
CH_3	$^{14}CH_4$	14.7		Dainton, Ivin, Wilkinson (70)
CH_3	CH_2O	6.2 6.6	4.39 4.58	Toby, Kutschke (73) Blake, Kutschke (74)
CH_3	CD_2O	7.9	4.48	Toby, Kutschke (73)
$n\text{-}C_3H_7$	$n\text{-}C_3H_7CHO^*$	6.7	4.3	Kerr, Trotman-Dickenson (75)
$n\text{-}C_3H_7$	$n\text{-}C_3H_7CHO^*$	10.8	4.3	Kerr, Trotman-Dickenson (75)
$iso\text{-}C_3H_7$	$iso\text{-}C_3H_7CHO^*$	6.3	4.3	Kerr, Trotman-Dickenson (76)
$iso\text{-}C_3H_7$	$iso\text{-}C_3H_7CHO^*$	9.5	4.2	Kerr, Trotman-Dickenson (76)
$n\text{-}C_3F_7$	H_2	12.3	5.64	Miller, Steacie (77)
$n\text{-}C_3F_7$	D_2	13.8 ± 0.5 12.9 ± 0.8	5.78	Miller, Steacie (77) Giacometti, Steacie (78)
$n\text{-}C_3F_7$	CH_4	9.5	3.99	Giacometti, Steacie (78)
$n\text{-}C_3F_7$	C_2H_6	9.2	5.24	Giacometti, Steacie (78)

* The H-atom which is italicized is abstracted.

of the data for the given radical and its fluorinated counterpart. Previous work has shown that the reactions of CH_3 with H_2, D_2, CH_4, C_2H_6, etc., have significantly higher values of $E_a - E_b/2$ than the corresponding reactions with CF_3 (71, 72). The recent data show that the H-abstraction reactions of n-C_3H_7 with aldehydes have E and A-factors analogous to those for H-abstraction from aldehydes by the CH_3 radical (75, 76); however, the values of $E_a - E_b/2$ for the n-C_3F_7 reactions with H_2 and D_2 are much greater than the values for the corresponding reactions with CF_3 or CH_3 (77, 78). This difference does not exist for the reaction of n-C_3F_7 with methane or ethane; here C_3F_7, like CF_3, is more reactive than CH_3. An adequate theoretical explanation of the activation-energy variations that occur with the nature of the attacking radical has not appeared. It is certainly evident that the relative magnitudes of the bond dissociation energies of the C—H bonds that are made and broken in the formation of the transition state, R—H—R', are not the only properties that must be considered in the development of a suitable theory of activation energies for these reactions.

By competitive rate studies Shaw & Trotman-Dickenson (79) have shown that the methoxyl radical is rather unselective in its H-abstraction reactions; they suggest that it is probably midway between that of CH_3 and Cl. The earlier data of Wijnen also indicate the high reactivity of the CH_3O radical (84).

Disproportionation and combination reactions of the free radicals.—Recently, estimates of the relative rates of reactions 14 and 15 have appeared for several of the simple free radicals. [R'(− H) represents an unsaturated molecule.]

$$R + R' \rightarrow RH + R'(- H) \qquad\qquad 14.$$

$$R + R' \rightarrow RR' \qquad\qquad 15.$$

These data are listed in Table II. Many investigators have found that the ratio, k_{14}/k_{15}, is relatively temperature independent ($E_{14} \cong E_{15}$), so that a comparison of data from experiments at different temperatures is partially justified. In any case, most of the results were obtained in experiments near room temperature. The major share of the estimates were derived by Boddy & Robb (85, 87, 88). They formed the ethyl, *iso*-propyl, *sec.*-butyl, and *tert.*-butyl radicals by the mercury photosensitized hydrogenation of the appropriate olefin, ethylene, propylene, butene-2, or isobutene. The initial radical formed in this fashion is energy-rich to the extent of 40 to 45 kcal. /mole, so that at low pressures k_{14}/k_{15} is very much higher than that found for thermally equilibrated radicals. "Hot" radical effects persist to rather high pressures (86), but a steady decrease in the observed ratio occurs as deactivation of the excited radical is effected. The data obtained from hydrogenation experiments that are shown in Table II were derived from extrapolation of the k_{14}/k_{15} ratio to infinite pressure, and they should represent data for thermally equilibrated radicals. In most cases where several independent estimates of the same ratio exist, the disagreement is great.

TABLE II

Disproportionation-Combination Ratio, k_{14}/k_{15}
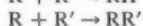
$$R + R' \rightarrow RH + R'(-H) \qquad 14.$$
$$R + R' \rightarrow RR' \qquad 15.$$

R	CH$_3$	C$_2$H$_5$	n-C$_3$H$_7$	iso-C$_3$H$_7$	sec.-C$_4$H$_9$	iso-C$_4$H$_9$	tert.-C$_4$H$_9$
R'							
C$_2$H$_5$	0.04(80) 0.06(81)	0.11(85) 0.14(86)	0.40(78)**	0.2(87)	—	—	0.3(87)
n-C$_3$H$_7$	0.05(82)*	—	0.16(75) 0.15(82)†	—	—	—	—
iso-C$_3$H$_7$	—	0.3(87)	—	0.65(76) 0.5(85)	0.4(87)	—	0.5(87)
sec.-C$_4$H$_9$	0.30(83)	—	—	0.4(87)	0.94(83) 1.5 (88) 2.3 (89)	—	2.0(87)
iso-C$_4$H$_9$	—	—	—	—	—	0.42(89)	—
tert.-C$_4$H$_9$	—	1.7(87)	—	1.2(87)	0.23(87)	—	2.2(88) 4.6(89)
CDO	~2.5(73)‡	—	—	—	—	—	—
CD$_3$O	1.4(84)	—	—	—	—	—	—

* R is CD$_3$, R' is CD$_2$CH$_2$CH$_3$.

† R and R' are CH$_3$CH$_2$CD$_2$.

‡ R is CD$_3$.

** The propyl radical in this case is n-C$_3$F$_7$.

Compare the results for sec.-butyl—sec.-butyl interaction; estimates of 0.94, 1.5, and 2.3 have been reported. The first two values were obtained by H-atom addition to olefin and the latter value from the photolysis of di-sec.-butyl ketone. There is also striking disagreement between the k_{14}/k_{15} estimates for the tert.-butyl—tert.-butyl interaction, 2.2 and 4.6. The first was obtained by H-atom addition to olefin and the second from ketone photolysis. In principle, both sets of data should be equally reliable. Although the estimates are not highly reproducible, one receives the unmistakable impression from the rather extensive data of Table II that there is no generality to the correlation observed earlier (80, 89) between the number of H-atoms that may be abstracted from a given radical to form an olefin product (or the probability of formation of the transition state for reaction 14) and the ratio k_{14}/k_{15}. Boddy & Robb reach this conclusion and also find no general relation between the k_{14}/k_{15} ratios and the exothermicities of the reactions. The most striking divergence from the simple probability picture (80, 89) is found in the data for the oxygen- or fluorine-containing radicals.

Although the magnitude of the ratios k_{14}/k_{15} for the pairs of reactions 14a-15a and 14b-15b, and for several other alkyl radical pairs, are in approximate agreement with the expectations based on equality of the combination rate constants and the simple probability picture $(k_{14a}/k_{15a} \cong 0.05, k_{14b}/k_{15b} \cong 0.13)$, this is far from the case for the CH_3—CH_3O, CH_3—CDO, and n-C_3F_7—C_2H_5 pairs:

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_4 \qquad\qquad 14a.$$
$$\rightarrow CH_3CH_2CH_3 \qquad\qquad 15a.$$
$$C_2H_5 + C_2H_6 \rightarrow C_2H_6 + C_2H_4 \qquad\qquad 14b.$$
$$\rightarrow C_4H_{10} \qquad\qquad 15b.$$
$$CH_3 + CH_3O \rightarrow CH_4 + CH_2O \qquad\qquad 14c.$$
$$\rightarrow CH_3OCH_3 \qquad\qquad 15c.$$
$$CH_3 + DCO \rightarrow CH_3D + CO \qquad\qquad 14d.$$
$$\rightarrow CH_3CDO \qquad\qquad 15d.$$
$$n\text{-}C_3F_7 + C_2H_6 \rightarrow C_3F_7H + C_2H_4 \qquad\qquad 14e.$$
$$\rightarrow C_3F_7C_2H_5 \qquad\qquad 15e.$$
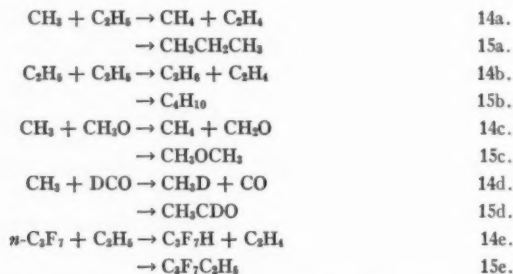
The ratios of k_{14}/k_{15} are 1.4, $\sim$2.5, and 0.40, respectively, for these reactions; about 0.05, 0.02, and 0.05, respectively, would be expected on the basis of the probability notion. Obviously other factors (such as dipole-dipole interactions) dominate in the case of the highly polar radicals. Kerr & Trotman-Dickenson (90) found that the ratio of the rate constants $k_{ab}/(k_{aa}k_{bb})^{1/2}$ for the radical combination reactions, $2A \rightarrow A_2$, $2B \rightarrow B_2$, $A+B \rightarrow AB$, is near 2.0 for a great variety of alkyl radicals reported in the literature. They suggest that the result must be regarded as an indication, though not as proof, that all these combinations occur on every collision. Although this case for alkyl radicals is somewhat convincing, the data of Wijnen (84) suggest that the same function of combination rate constants for the pair, CH_3O and CH_3, is much less than the 2.0 value common to the alkyl radical reactions. For the case of combinations between highly polar radicals, such as CH_3O, the rate of association may be appreciably slower than is common for the non-polar alkyl radicals.

Free radical addition reactions.—Kinetic data for several of the simple alkyl radical addition reactions with ethylene, reported in the past year, are summarized in Table III. The striking difference between the rate data for CH_3 and C_2H_5 radicals is rather unexpected and unexplained. King & Steacie (93) have photolyzed CF_3CN and derived the rate data, $k_{16}/k_{18}^{1/2} = 10^{-9.1}$ exp $(-5.0$ kcal./$RT)$ (cc./molecule-sec.)$^{1/2}$.

$$CF_3 + CF_3CN \rightarrow (CF_3)_2CN \qquad\qquad 16.$$
$$(CF_3)_2CN + CF_3 \rightarrow (CF_3)_2C{=}NCF_3 \qquad\qquad 17.$$
$$2CF_3 \rightarrow C_2F_6 \qquad\qquad 18.$$
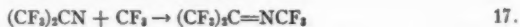
Several interesting studies of the addition of methylene radical to olefins have appeared. Frey has photolyzed diazomethane and studied the

TABLE III

Free Radical Addition to Ethylene

$$R + C_2H_4 \rightarrow RC_2H_4 \qquad a.$$
$$2R \rightarrow R_2 \qquad b.$$

R	E_a-$E_b/2$, kcal./mole	$\log (A_a/A_b^{1/2})$ (A, cc./mole-sec.)	Investigator
CH_3	8.7	5.41	Brinton (91)
C_2H_5	5.5	3.31	Lampe, Field (92)
n-C_3H_7	6.5	3.9	Kerr, Trotman-Dickenson (75)
iso-C_3H_7	6.9	4.4	Kerr, Trotman-Dickenson (76)

competitive attack of CH_2 on the C—H and the C=C bonds in isobutene (94) and *cis*- and *trans*-butene-2 (95). The stereospecificity of the reaction of CH_2 with the *cis*- and *trans*-butenes confirms the singlet state for methylene (96).

Free radical decomposition reactions.—The decomposition reactions of the *n*-propyl, *iso*-propyl, and *sec.*-butyl free radicals have been reinvestigated recently. The rate data are compared in Table IV. The new data for the reaction 19a support a higher value for E_{19a} than the

$$n\text{-}C_3H_7 \rightarrow CH_2CH_2 + CH_3 \qquad 19a.$$

earlier results suggested. Some possible difficulties in the interpretation of the earlier work have been reviewed (99). The reasons for the very great

TABLE IV

Free Radical Decomposition Reactions

$$R \rightarrow R' + A \qquad 19.$$
$$2R \rightarrow R_2 \qquad 20.$$

Reaction 19	E_{19}-$E_{20}/2$, kcal./mole	$\log (A_{19}/A_{20}^{1/2})$ (A, cc./mole-sec.)	Investigator
$CH_3CH_2CH_2 \rightarrow CH_3 + CH_2CH_2$	25.2	4.7	Kerr, Trotman-Dickenson (75)
	34.9	8.78	Calvert, Sleppy (97)
$CH_3CH_2CH_2 \rightarrow H + CH_3CH=CH_2$	35.0	6.6	Kerr, Trotman-Dickenson (75)
$CH_3CHCH_3 \rightarrow CH_3 + CH_2CH_2$	29.5*	3.6*	Kerr, Trotman-Dickenson (76)
	32.5	5.03†	Heller, Gordon (98)
$CH_3CHCH_3 \rightarrow H + CH_2CH=CH_2$	36.9	6.8	Kerr, Trotman-Dickenson (76)
$CH_3CHCH_2CH_3 \rightarrow CH_3 + CH_3CH=CH_2$	30.6	8.66	Gruver, Calvert (99)

* Based on C_2H_4 yield; CH_4 rate data give E_{19}-$E_{20}/2 = 27.1$; $\log (A_{19}/A_{20}^{1/2}) = 3.3$.
† Value as recalculated by Kerr & Trotman-Dickenson (76) from data of Heller & Gordon.

difference between the recent estimates is not clear. Both of the studies were based upon relatively uncomplicated reaction systems, the high temperature photolysis of n-butyraldehyde (75) and the azomethane photosensitized decomposition of n-butyraldehyde (97). The rate constants are in fair agreement for the temperatures common to both studies, but the temperature dependence of rate constants is greatly different. It is possible that complications related to the transition of 19a from the second- to the first-order region of kinetics cause this difference; rather different pressures of reactants were employed in the two studies. The "high" values of E_{19a} coupled with recent estimates of E_{-19a} are in reasonable accord with the probable value of ΔH_{19a} based on "reasonable" thermal data.

Until recently it has been the common opinion that H-atom migration in alkyl free radicals was immeasurably slow in the gas phase. Heller & Gordon (98) first presented evidence for the occurrence of this type of reaction; 19b was proposed. Kerr & Trotman-Dickenson have recently

$$CH_3CHCH_3 \rightarrow CH_2CH_2 + CH_3 \qquad\qquad 19b.$$

considered the occurrence of 19b in explanation of the products of iso-butyraldehyde photolysis at elevated temperatures (76). The agreement between the independent kinetic data related to 19b is not good, but no poorer than that for many other generally accepted reactions. However, there are several facts that leave one rather uncertain concerning the suggested importance of 19b; first, the analogous decomposition of $sec.$-butyl radicals is immeasurably slow under similar conditions (100); second, the reaction 19b and its analogues have not been observed by Lossing & deSousa (101) in mass spectrometric studies of the decomposition of iso-C_3H_7, $sec.$-C_4H_9, iso-C_4H_9, and $tert.$-C_4H_9 radicals in the range 350–525°C.

Gordon & McNesby (102) have followed the product distribution from the photolysis of CD_3COCD_3-C_2H_4 mixtures from 300–500°C. They have shown that the primary radicals, n-pentyl, n-hexyl, and n-heptyl, isomerize efficiently at temperatures above 250°C., although n-butyl does not isomerize up to 500°C. (100). The isomerization is the result of an internal H-abstraction reaction; for the n-pentyl radical, the reaction 21 is proposed; at high temperatures this is followed by the rapid reaction 22. The authors suggest that this is the major mode of

$$CD_3CH_2CH_2CH_2CH_2^{\cdot} \rightarrow CD_3C^{\cdot}HCH_2CH_2CH_3 \qquad\qquad 21.$$
$$CD_3C^{\cdot}HCH_2CH_2CH_3 \rightarrow CD_3CH{=}CH_2 + C_2H_5^{\cdot} \qquad\qquad 22.$$

reaction of long chain radicals since it is unimolecular and probably of low activation energy ($E_{21} \cong 9$ kcal.). The experimental evaluation of A_{21} and E_{21} would be most interesting. In an analogous study, Gordon, Smith & McNesby (103) found that cyclopentyl radicals decompose readily by reaction 23 at temperatures above 250°C. Above 450°C. the allyl radical partic-

$$\overline{CH_2CH_2CH_2CH_2C^{\cdot}H} \rightarrow C_2H_4 + CH_2{=}CHCH_2^{\cdot} \qquad\qquad 23.$$
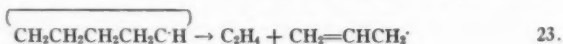
ipates in a H-abstraction reaction 24. They estimate $E_{24} = 31.8 \pm 3.6$ kcal.

$$CH_2{=}CHCH_2 \cdot + cyclo\text{-}C_6H_{10} \rightarrow CH_3CH{=}CH_2 + \overbrace{CH_2CH_2CH_2CH_2C\cdot H} \qquad 24.$$
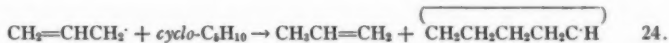
Some interesting studies of the reactions of excited radicals and molecules have been reported in the past year. Rabinovitch & Diesen (83) have formed chemically activated *sec.*-butyl radicals by the reaction of H-atoms with *cis*-butene-2. The ratios of rates of stabilization versus decomposition by C—C bond rupture for the energized butyl radicals were measured as a function of pressure and temperature. Application of the theory of unimolecular reaction rates showed that all vibrational degrees of freedom may be taken as active. Rabinovitch, Tschuikow-Roux & Schlag (104) have followed the relative rates of isomerization and stabilization of vibrationally excited *trans*-cyclopropane-d₂ formed by CH_2 addition to *trans*-ethylene-d₂. Results up to 36 atm. pressure appear consistent with theory. Rabinovitch & Michel (105) followed the rate of the *cis-trans* isomerization of *cis*-butene-2 at temperatures in the range 414–469°C. and pressures from 5×10^{-3} to 100 mm. of butene and up to 2000 mm. of nitrogen. The results appear consistent with the Slater theory.

Cashion & Polanyi (106, 107) have reported preliminary results of the measurement of the infrared chemiluminescence from excited radicals and molecules that are formed on reaction of H-atoms with O_2 or NO at room temperature. In these very interesting experiments they hope to characterize the energy distribution of the initial products.

The mechanism of the very unusual deuterium exchange in methyl radicals has been restudied by Ivanov, Fok & Voevodskii (108). CH_3 radicals are formed in the Polanyi sodium flame reaction, $CH_3I + Na \rightarrow NaI + CH_3$, and react with D_2 carrier. The authors conclude that the sodium metal surface seems to play some role. Lossing & deSousa (101) report a convenient high-temperature source of any desired alkyl radical, R, which appears to be free from structural ambiguity and undesirable side reactions. The pyrolysis of the structurally related nitrite, RCH_2ONO, gives a clean source of R from 350–525°C.:

$$RCH_2ONO \rightarrow RCH_2O + NO; \quad RCH_2O \rightarrow R + CH_2O.$$

Reactions of radicals with the oxides of nitrogen.—-The reaction of CH_3 with NO has been restudied recently. Christie has reported two very interesting studies (109, 110). She prepared CH_3 radicals through the photolysis of methyl iodide. The addition of nitric oxide markedly increases the quantum yield of iodine, since this yield is determined by a competition between the iodine and nitric oxide for methyl:

$$CH_3 + I_2 \rightarrow CH_3I + I \qquad\qquad 25.$$

$$CH_3 + NO(+ M) \rightarrow CH_3NO(+ M) \qquad 26.$$
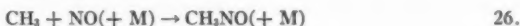
From relative rates of 25 and 26 Christie finds that the apparent third-order constant for 26 is 50 times as great as that measured for the similar reaction of CH_3 with O_2 (109), and the limiting value of the apparent second-order rate constant $k_{26} \cong 7 \times 10^{11}$ cc./mole-sec. (within a factor of three) for temperatures near 20°C.; this is in excellent agreement with the second-order rate constant derived independently by Sleppy & Calvert (111). They studied the competitive rates of methyl combination and reaction 26 in the flash photolysis of azomethane-nitric oxide-neopentane mixtures (170 to 290 mm.) and estimate $k_{26} = 6.3 \times 10^{11}$ cc./mole-sec. for 25°C. Also in this study it was confirmed that the CH_3 reaction with O_2 follows *third*-order kinetics in the same pressure region (111). It seems well established that there is a marked difference in the lifetimes of the two 6-atom complexes, CH_3O_2' and CH_3NO'. Christie suggests that the CH_3O_2' complex is "loose" with free rotation of components, while the CH_3NO' complex is "rigid." According to the theory of Marcus & Rice (112), a "loose" complex would show a marked pressure dependence but no steric effect, but for a "rigid" complex, a small pressure dependence over the same pressure range and a marked steric effect are expected. In their rationalization of the results, Sleppy & Calvert employ the presumed difference in exothermicities of the two reactions and the expectations based on the Rice-Ramsperger-Kassel classical model (113). Christie (110) reported that nitrosomethane reacts when in the presence of excess NO to form a highly absorbing unknown compound Y (possibly $CH_3(NO)_3$). The rate law, $d[Y]/dt = k[CH_3NO][NO]^2$, is followed. In the absence of excess NO the nitrosomethane disappears by a second-order rate law; $d[CH_3NO]/dt = k[CH_3NO]^2$, where $k \cong 1.2 \times 10^4$ cc./mole-sec. at room temperature.

Kenwright & Trenwith (114) studied the N_2O-C_2H_6 reaction in the range 553–588°C. In combination with other rate data their results give $k_{27} = 6 \times 10^{14}$ exp $(-31$ kcal./$RT)$ l./mole-sec.

$$C_2H_6 + N_2O \rightarrow C_2H_5O + N_2 \qquad 27.$$

From a kinetic study of the photolysis of ammonia in the presence of nitric oxide, Serewicz & Noyes (115) have derived a rate constant function involving reactions 28, 29, and 30:

$$H + NO \rightarrow HNO \qquad 28.$$
$$2\,HNO \rightarrow N_2O + H_2O \qquad 29.$$
$$H + HNO \rightarrow H_2 + NO \qquad 30.$$

For runs at 31°C., $k_{28}k_{29}^{1/2}/k_{30} = 1.3 \pm 0.1 \times 10^3$ (l./mole-hr.)$^{1/2}$ Cashion & Polanyi (107) have observed the infrared chemiluminescence from the excited HNO molecule formed at low pressures. If $E_{28} = 0$, then the minimum wavelength of the emission suggests $D_{H-NO} \geq 46$ kcal./mole.

Oxidation studies at low temperatures.—The difficulties related to the study of oxidations seem several magnitudes greater than those encountered in the usual kinetic studies. The transient nature of some products, the

complexity and number of the final products, major uncertainties in the choice between alternative mechanisms, etc., all tend to make significant progress in this area very slow. Noyes has recently published an interesting account of many of the problems related to the study of low-temperature oxidations in photochemical systems (116). Gray & Williams have derived from current data thermodynamic constants for the hydroxyl (117), hydroperoxyl (117), and the alkoxyl radicals (118, 119) which should prove most useful to kinetic workers in this field. A considerable number of researchers have followed the lead of the University of Rochester research group and studied the reaction of alkyl radicals (formed photochemically) with oxygen at low temperatures. These studies are considerably less complicated than the more common high-temperature oxidation studies, but whether the information gained under these conditions has any value whatever in the illucidation of the mechanisms at high temperature is open to question.

Several independent studies related to the methyl radical oxidation have appeared. The methyl radicals were generated by the photolysis of azomethane (111; 120 to 122) or acetaldehyde (123). The non-specialist may be surprised to find that even in the case of the very simple methyl radical there is still considerable uncertainty as to the detailed oxidation reactions. CH_3O_2 is presumed to be the primary product of the CH_3-O_2 interaction at low temperatures; it would probably be agreed generally that the kinetics of its formation follow the equation, $CH_3+O_2+M \rightarrow CH_3O_2 +M$, in the usual pressure region. But how the CH_3O_2 radical is converted to the final observed products of the reaction remains a matter of considerable uncertainty. Oxidation studies at higher temperatures have continued to constitute a major research effort in the field of reaction kinetics. Space limitations do not allow reference to this work. The magnitude of the field and the wide interest in it would justify separate consideration in a future volume.

Four books on the properties and reactions of free radicals which may be of interest to kineticists have appeared during 1959 (124 to 127, 180). Two independent translations of both volumes of Semenov's kinetics book are available (125, 126).

CHEMICAL REACTIONS OF MOLECULES

Molecular decompositions.—Recent rate data for first-order thermal decomposition reactions are listed in Table V. The data refer presumably to the rate of the individual primary steps listed in Table V. The "high" pre-exponential factors for a number of simple bond cleavage processes are evident. It is rather surprising that the rate of 4-bromopent-1-ene decomposition is essentially the same as that found earlier by Kale, Maccoll & Thomas (138) for *sec.*-butyl bromide decomposition ($k = 3.39 \times 10^{13}$ exp (-46.4 kcal./RT) sec.$^{-1}$). From this fact Thomas (132) concludes that the rate determining step (which presumably involves a four-center transition state) is concerned solely with the activation of the C—Br bond; the breaking of the

TABLE V

RATE DATA FOR FIRST-ORDER MOLECULAR DECOMPOSITIONS

Reaction	$\log(A, sec.^{-1})$	$E_a,$ kcal./mole	Investigator
$CH_3NO_2 \rightarrow CH_3 + NO_2$	13.73	49.2	Makovky, Gruenwald (128)
$(CH_3)_2Hg \rightarrow CH_3Hg + CH_3$	15.70	57.9	Russell, Bernstein (129)
$(CH_3)_2N_2 \rightarrow CH_3N_2 + CH_3$	15.7	51.2	Steel, Trotman-Dickenson (130)
$CH_2OOCH_2 \rightarrow 2CH_2O$	15.20	35.3	Hanst, Calvert (131)
$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO$	16.40	38.7	Blake, Kutschke (74)
$CH_3CH_2Br \rightarrow CH_2CH_2 + HBr$	13.45	53.9	Thomas (132)
$CH_3CH(NO_2)CH_3 \rightarrow CH_3CH{=}CH_2$ + HNO_2	11.05	39.3	Smith, Calvert (133)
$CH_2{=}CHCH_2CHBrCH_3 \rightarrow HBr$ + $CH_2{=}CHCH{=}CHCH_3$	12.94	44.7	Thomas (132)
$(CH_3)_3COH \rightarrow (CH_3)_2C{=}CH_2 + H_2O$	11.51	54.5	Barnard (134)

C—H bond and formation of the conjugated diene system occur in some later non-rate-determining step. Guenther & Walters (139) have found that the kinetics of CO_2 formation in the thermal decomposition of ketene is described adequately by the bimolecular reaction, $2CH_2{=}CO \rightarrow CO_2 + CH_2{=}C{=}CH_2$. Crocco, Glassman & Smith (140) have described a new flow reactor for high-temperature kinetic studies. The reaction of ethylene oxide decomposition was followed near 927°C. by tracing only the temperature history of the reaction. The "first-order" constant for the decomposition fits the relation, $k = 1 \times 10^{11} \exp(-42 \text{ kcal.}/RT) \text{ sec.}^{-1}$.

Russell & Bernstein (141) have determined the ratio of the rate constant for the decomposition of $Hg(^{12}CH_3)_2$ to that for $(^{12}CH_3)Hg(^{13}CH_3)$. For the fully inhibited reaction at the high pressure limit the ratio is 1.034 ± 0.002, independent of the temperature. The Bigeleisen simplified equation (142, 143) predicts a ratio of 1.023, assuming a single C—Hg bond rupture in the primary act. New studies of the thermal decompositions of dimethyl ether (144), diethyl ether (145), dichloromethane (146), methane (147), and oxygen (148, 149) have appeared. The experimental activation energy obtained by Skinner & Ruehrwein in the shock tube pyrolysis of CH_4 is 101 kcal./mole; this suggests that $CH_4 \rightarrow CH_3 + H$ is the initiating reaction and the chain length is only 2 (147). Losev's shock tube dissociation of O_2 at high temperatures gives $k = 3 \times 10^{12} T^{1/2} \exp(-99.2 \text{ kcal.}/RT)$ cc./mole-sec., which is assigned to the reaction, $O_2 + O_2 \rightarrow O_3 + O$ (149).

Bose & Hinshelwood (150) have extended the study of Birss (151) on the halide acceleration of the rate of decomposition of di-*tert.*-butyl peroxide. The order of effectiveness of the fluorides is $SiF_4 > SF_6 > CF_4$, the inverse ease with which they release F-atoms. Complex formation is not consistent with the observations, but the mechanism is discussed in relation to an extended theory of unimolecular reactions.

Thermal reactions between molecules.—Rate data of several systems are summarized in Table VI. Sullivan's reinvestigation of the hydrogen-iodine

TABLE VI

Rate Data for Second-Order Molecular Reactions

Reaction	log $(A$, cc. /mole-sec.)	E_a, kcal./mole	Investigators
$H_2O_2 + H_2O_2 \rightarrow 2\ OH + H_2O_2$	18.4	48.0	Hoare, Protheroe, Walsh (135)
$NO + NO \rightarrow N_2 + O_2$	13.49	63.1	Yuan, Slaughter, Koerner, Daniels (136)
$NO_2 + Ar \rightarrow NO + O + Ar$	16.49	65.4	Huffman, Davidson (137)
$NO_2 + NO_2 \rightarrow 2NO + O_2$*	13.40	25.0	Huffman, Davidson (137)

* There may be some other mechanism here besides the "Bodenstein bimolecular" path.

reaction at temperatures from 360°–465°C. (152) has confirmed the suggestion of Benson & Srinivasan (153) that free atoms participate in the reaction. This classical reaction has long been considered as the typical bimolecular reaction involving a four-center complex. However, a free atom process, reactions 33 to 37, accounts for 10 per cent of the overall reaction at 360° and 27 per cent at 465°C.

$$H_2 + I_2 \rightarrow 2HI \qquad\qquad 31.$$
$$2HI \rightarrow H_2 + I_2 \qquad\qquad 32.$$
$$I_2 \rightleftharpoons 2I \qquad\qquad 33.$$
$$I + H_2 \rightarrow HI + H \qquad\qquad 34.$$
$$H + HI \rightarrow H_2 + I \qquad\qquad 35.$$
$$H + I_2 \rightarrow HI + I \qquad\qquad 36.$$
$$I + HI \rightarrow I_2 + H \qquad\qquad 37.$$
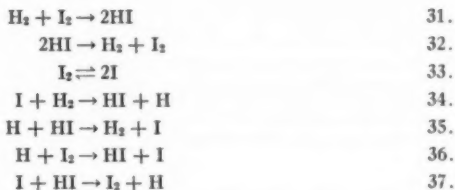
The data give: log $(k_{31}/T^{1/2}) = 12.78 - (40.7\ \text{kcal.})/4.575T$; log $(k_{34}/T^{1/2}) = 12.75 - 33.4/4.575T$; $k_{35}/k_{36} = 0.07$, 0.082, 0.117, and 0.125 at 360, 394, 437, and 465°C., respectively. In terms of this combined molecular and atomic mechanism there is no inconsistency in the rates of the HI formation and destruction reactions at equilibrium (154).

The short wavelength limit of the radiation (16,935 cm.$^{-1}$) from excited NO_2 formed in the reaction, $O_3 + NO \rightarrow NO_2* + O_2$, has been found by Greaves & Garvin (155) to be close to the enthalpy change for the reaction (47.5 kcal./mole). The problem of the slowness of the NH_3—BF_3 reaction compared to other BF_3-amine reactions has been reconsidered (156).

PHOTOCHEMISTRY

Primary processes in direct photodecompositions.—Some very interesting new information on the nature of the primary photochemical processes is summarized in Table VII. Recent data from the W. A. Noyes research group have clarified the detailed mechanism of the Norrish "type II" primary process in ketone photolysis (82, 157, 158). This primary mode of photodecomposition in the photolysis of 2-hexanone involves the formation of propylene and acetone (as final products). The quantum yield of these products is relatively unaffected by the presence of oxygen or by temperature

TABLE VII

PRIMARY PROCESSES IN DIRECT PHOTODECOMPOSITIONS

Primary Process	Wave Length, A	Investigators
$CH_3OH + h\nu \rightarrow CH_2O + H_2$	<2000	Porter, Noyes (159)
$\rightarrow CH_3O + H$		
$CH_2CH_2CH_2O + h\nu \rightarrow CH_2O + CH_2CH_2$	<2000	Margerum, Pitts, Rutgers, Searles (160)
$CH_2CH_2C(CH_3)_2O + h\nu \rightarrow CH_3COCH_3 + CH_2CH_2$	<2000	Margerum, Pitts, Rutgers, Searles (160)
$\rightarrow CH_2O + (CH_3)_2C=CH_2$		
$CH_3CH_2CH_2COCH_3\dagger + h\nu \rightarrow CH_2CH_2 + CH_2=C(OH)CH_3^*$	Full Hg arc	Ausloos, Murad (82)
$CH_3CH_2CD_2COCD_3 + h\nu \rightarrow CH_2CH_2 + CD_2=C(OH)CD_3^*$	Full Hg arc	Ausloos, Murad (82)
$CH_3COCH_2CH_2CH_2CH_3 + h\nu \rightarrow C_3H_6 + CH_2=C(OH)CH_3^*$	3130	Brunet, Noyes (157) Srinivasan (158)
$CH_3COCH_2CH_2CD_2CH_3 + h\nu \rightarrow C_3H_5D + CH_2=C(OD)CH_3^*$	3130	Srinivasan (158)
$CH_2CH_2CH_2CH_2CO + h\nu \rightarrow CH_2=CHCH_2CH_2CHO$	3130	Srinivasan (161)
$CD_2CH_2CH_2CD_2CO + h\nu \rightarrow CD_2=CHCH_2CD_2CHO$	3130	Srinivasan (161)
$CH_2CH_2CH_2CH_2CH_2CO + h\nu \rightarrow CH_2=CHCH_2CH_2CH_2CHO$	3130	Srinivasan (162)
$CH_3CH_2CH_2CH_2CH(CH_2)CO + h\nu$		
$\rightarrow CH_3CH=CHCH_2CH_2CH_2CHO$	3130	Srinivasan (162)

* Strong indirect evidence is presented that this enol-acetone is the primary product, although ordinary acetone is found on analysis of the condensed products.

† For this and each of the ketones a large fraction of the excited molecules decompose into free radicals; these primary modes of photodecomposition were not of primary concern in these studies, and the processes have been omitted here.

variation. Thus, the decomposition is presumed to proceed from an excited singlet state of the ketone molecule. The D-tracer experiments of Srinivasan (158) present the strongest evidence that a cyclic 6-membered transition state is involved in the decomposition and that the enol-form of acetone is one of the primary products. This mechanism has been assumed in the formulation of the primary processes shown in Table VII. Srinivasan has discovered somewhat similar new modes of primary photodecomposition for cyclopentanone (161) and cyclohenanone (162).

Gordus & Bernstein (163) have studied the relative rates of formation of the isotopic radicals $^{12}CH_3$, $^{13}CH_3$, and CD_3 in the photolyses of the corresponding methyl bromide isotopic molecules. The C^{12}/C^{13} enrichment factor was 1.039 ± 0.003. The corresponding factor for the $^{12}CH_3^{12}CH_2$ and $^{12}CH_3^{13}CH_2$ formation from ethyl bromide was 1.041 ± 0.004. The CH_3/CD_3 fractionation factor was 1.41 ± 0.01. The difference in photodecomposition rates is attributed to a difference in the extinction coefficients of the bromides; in the case of deuterium-labeled compound this was proven experimentally, $\alpha_{CH_3Br}/\alpha_{CD_3Br} = 1.38 \pm 0.05$.

Heicklen & Noyes (164, 165) have restudied the fluorescence and phosphorescence of biacetyl and acetone. They have found that an efficient transfer of energy occurs between excited acetone molecules and biacetyl. This results in a marked dependence of quantum yields of decomposition

of acetone on the time of irradiation; thus it seems that kinetic data from extended acetone photolyses (particularly for experiments at the lower temperatures) must be reinterpreted carefully. The mechanisms of deactivation of electronically excited ketene (166) and hexafluoroacetone (167) have been reinvestigated in the past year. The mechanism of SO_2 and SO_3 photolysis has been restudied by means of flash photolysis (168). Beckey & Groth (169) gave a preliminary report of the first success in the identification of the acetyl radical from the direct photolysis of acetone vapor; the experiments were carried out with the aid of the field emission-ion source mass spectrometer.

Primary reaction modes in the mercury photosensitized reactions.—The appearance of two independent series of research papers has added greatly to our knowledge of the primary acts in mercury photosensitized reactions. Using a ^{202}Hg-containing, low-pressure, resonance lamp, Gunning and co-workers have studied the reactions of $^{202}Hg(^3P_1)$ atoms excited in natural mercury (Hg^N). Reactions of $^{202}Hg(^3P_1)$ with H_2O, N_2O, O_2, (170), HCl (171, 173), CH_3Cl (172), and iso-C_3H_7Cl (172) were followed in a flow system by determining the extent of enrichment of the ^{202}Hg isotope in the oxide or calomel product. In the reaction with HCl (with added butadiene) at 28–30°C., enrichments up to 98 per cent ^{202}Hg in the calomel were obtained (171, 173); 29.8 per cent of the ^{202}Hg isotope occurs in natural mercury. Lower enrichments are found in static systems, in experiments without added olefin, at high pressure, or at high temperature. The experiments are explicable in terms of the sequence:

$$^{202}Hg(^3P_1) + HCl \rightarrow {}^{202}HgCl + H \qquad 38.$$
$$^{202}Hg(^3P_1) + HCl \rightarrow {}^{202}Hg + H + Cl \qquad 39.$$
$$Cl + Hg^N + M \rightarrow Hg^NCl + M \qquad 40.$$
$$H + HCl \rightarrow H_2 + Cl \qquad 41.$$
$$Cl + olefin \rightarrow Product \qquad 42.$$
$$H + olefin \rightarrow Product \qquad 43.$$
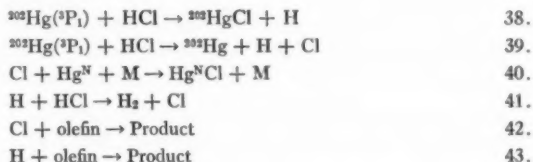
In the presence of olefin, reactions 42 and 43 remove the active atoms that normally tend to lower the enrichment by reaction 40. The ratio of the quantum yield of reaction 38 to that of 39 is 0.40 ± 0.02. Decreased enrichment at high pressures is a consequence of Lorentz-broadening, which causes an overlap of the hyperfine absorption structure of the mercury isotopes. Cvetanović, Gunning & Steacie have found that there is a pronounced interaction between $Hg(^3P_1)$ atoms and olefinic double bonds (174). They determined the extent of isomerization of *cis*-2- and *trans*-2-butenes induced by reaction with $Hg(^3P_1)$ atoms. Regardless of the starting material, prolonged reaction produced equimolar mixtures of *trans*- and *cis*-isomers. The primary step is proposed to be the uncoupling of the two π-electrons of the double bond, with formation of highly excited triplet states.

Lossing and co-workers have determined the primary modes of reaction

of $Hg(^3P_1)$ atoms with a variety of molecules by direct or indirect observation of the primary radicals or products formed in a modified mass spectrometer. Summarized below are the suggested major modes of reaction with formic acid (175), methyl formate (175), acetic acid (175), biacetyl (176), acetylacetone (176), acetonyl acetone (176), benzaldehyde (177), acrolein (177), and crotonaldehyde (177).

$$HCO_2H + Hg(^3P_1) \rightarrow H_2O + CO + Hg(^1S_0)$$
$$\rightarrow H_2 + CO_2 + Hg(^1S_0)$$
$$HCO_2CH_3 + Hg(^3P_1) \rightarrow HCO + OCH_3 + Hg(^1S_0)$$
$$\rightarrow H + CO_2CH_3 + Hg(^1S_0)$$
$$CH_2CO_2H + Hg(^3P_1) \rightarrow CH_2CO + OH + Hg(^1S_0)$$
$$\rightarrow CH_3 + CO_2H + Hg(^1S_0)$$
$$\rightarrow CH_4 + CO_2 + Hg(^1S_0)$$
$$\rightarrow H_2O + CH_2=CO + Hg(^1S_0)$$
$$(CH_3CO)_2 + Hg(^3P_1) \rightarrow 2CH_3CO + Hg(^1S_0)$$
$$CH_3COCH_2COCH_3 + Hg(^3P_1) \rightarrow CH_3CO + CH_2COCH_3 + Hg(^1S_0)$$
$$CH_3COCH_2CH_2COCH_3 + Hg(^3P_1) \rightarrow CH_3CO + CH_2CH_2COCH_3(or\ CH_2\dot{C}HCOCH_3)$$
$$+ Hg(^1S_0)$$
$$C_6H_5CHO + Hg(^3P_1) \rightarrow C_6H_6 + CO + Hg(^1S_0)$$
$$\rightarrow C_6H_5 + HCO + Hg(^1S_0)$$
$$\rightarrow Polymer$$
$$CH_2=CHCHO + Hg(^3P_1) \rightarrow CH_2CH_2 + CO + Hg(^1S_0)$$
$$\rightarrow CH_2=CH + CHO + Hg(^1S_0)$$
$$\rightarrow CH_2=CHCO + H + Hg(^1S_0)$$
$$CH_3CH=CHCHO + Hg(^3P_1) \rightarrow CH_3CH=CHCO + H + Hg(^1S_0)$$
$$\rightarrow C_3H_6 + CO + Hg(^1S_0)$$

Two reinvestigations of the kinetics and mechanism of the interaction of $Hg(^3P_1)$ atoms with oxygen have appeared (178, 179).

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PHYSICAL ORGANIC CHEMISTRY[1]

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Books and reviews.—Recent books of interest to physical organic chemists include: Bell (1), de la Mare & Ridd (2), Gould (3), Ingold (4), Staab (5), Trotman-Dickenson (6), Hückel (7), the papers presented to the Kekulé Symposium (8), Waters (9), and Gray (10). The following topics have been reviewed elsewhere during the year: the mechanisms of epoxide reactions (11), the thermochemistry and reactivity of alkoxyl radicals (12), carbenes (methylenes) as reaction intermediates (13), organic catalysts (14), hyperconjugation (15 to 30), and the Willgerodt-Kindler reaction (31).

FREE RADICAL REACTIONS

Although it has certainly seemed probable for some time that the free radical arylation of benzene derivatives involves an initial addition to the benzene ring to give an arylcyclohexadienyl radical, this mechanism has been placed on an even firmer basis by DeTar & Long's isolation of a dimerization product of this radical (32). This observation is analogous to the reports of the isolation of intermediate-radical-dimerization products in the reactions of anthracene with various radicals (33, 34).

In agreement with the general belief that the vapor-phase nitration of alkanes is a free-radical process, Hughes, Ingold, and co-workers have noted that when the vapor-phase nitration of *t*-butylbenzene is carried out in the presence of an inert gas (to give the intermediate radicals a longer average life-time), products resulting from the rearrangement of the 2-methyl-2-phenylpropyl (neophyl) radical are found (35). They further observe that even in the chlorination of *t*-butylbenzene, where rearrangement had not been found previously, the vapor-phase reaction gave considerable amounts of rearranged product (36).

Hiatt & Bartlett have carried out a study of the thermal reaction of styrene with ethyl thioglycolate that gives added evidence that the thermal polymerization of styrene is initiated by a third-order reaction (37).

Benson & North have devised a new method for determination of the absolute rate constants for propagation and termination in chain reactions (38).

Bartlett, Trifan & Fraenkel have found that in the absence of inhibitors,

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[1] The literature search for this review was completed on December 1, 1959. The arbitrary restrictions made by the reviewer to keep the review within the allotted length include the omission of reference to all but a few articles published before late 1958.

iodine adds to styrene (reversibly) by a free-radical chain process, that a slower polar addition persists when the radical reaction is completely inhibited and that at iodine concentrations above 20 per cent a cationic polymerization occurs (39, 40).

Grovenstein *et al.* have shown that alkyl groups are cleaved from tetraalkylammonium ions by metallic sodium in dioxane (41) or liquid ammonia (42) to extents that suggest that methyl and primary groups are removed as carbanions and secondary and tertiary groups are removed as radicals.

Peroxide decompositions.—Bartlett & Hiatt have presented a convincing argument that the thermal decomposition of certain *t*-butyl peresters is a concerted process involving the simultaneous cleavage of two or more bonds (43). At 60°, where the decomposition of di-*t*-butyl peroxide has a half-life of about 10^7 min. and that of benzoyl peroxide a half-life of 6000 min., the *t*-butyl peresters studied by these workers had half-lives as shown in Table I.

TABLE I

DECOMPOSITION RATES OF PERESTERS $RCO_2OC(CH_3)_3$ AT 60°

R	Half-life (min.)	ΔH‡ (kcal.)	ΔS‡ (cal./degree)
Methyl	500,000	38	17
Phenyl	30,000	33.5	7.8
Benzyl	1,700	28.7	3.9
Trichloromethyl	970	30.1	8.9
t-Butyl	300	30.6	13
3-Phenylallyl	100	23.5	−5.9
Benzhydryl	26	24.3	−1.0
2-Phenyl-2-propyl	12	26.1	5.8
1,1-Diphenylethyl	6	24.7	3.3
1-Phenylallyl	4	23.0	−1.1

The strong tendency for the reaction rate to increase with the stability of the R groups (as radicals) listed in Table I suggests that these R's are indeed becoming radicals in the transition states of these reactions. A sort of saturation effect is noted, in that a given activating structural change (such as the replacement of an α-methyl group by phenyl) has a greater effect when it is made in a less reactive perester. This is the opposite of what would be expected if the substituent effects were steric in nature with the larger groups increasing the reactivity. The saturation effect probably results from the fact that as the stability of the radical R being formed increases, the transition state occurs earlier in the bond-cleavage process so that less of the increased stability is reflected in the reaction rate. Bartlett & Hiatt account for the observed tendency for the activation energy to decrease with the activation enthalpy very plausibly in terms of the increase in number of bonds around which rotation must be frozen if resonance stabilization of the radical being

formed in the transition state is to be at a maximum. The greater reactivity in the case R = 1-phenylallyl compared to the case R = 3-phenylallyl, wherein the same radical is being formed, is also attributed to differences in degrees of rotational freedom. The fact that the unconjugated perester must have a higher energy content than its conjugated isomer, which yields the same product, must also be an important cause of this difference in reactivities.

The decomposition of $(RCO_2)_2$, where R is a primary radical, appears to be a borderline case. DeTar & Lamb have found that the rate of decomposition of δ-phenylvaleryl peroxide is not fast enough to prove that any more favorable reaction path has been able to supersede the simple O—O bond cleavage that appears to be characteristic of at least the major part of the spontaneous decomposition of acetyl and benzoyl peroxides (44). They have, however, given evidence of another type indicating that at least a considerable amount of the decomposition reaction involves the simultaneous cleavage of two or three bonds. Their observation that the presence of water and iodine decreases the yield of carbon dioxide from 1.7 to 1.4 moles per mole of peroxide shows that at least 0.3 mole of phenylvaleroxy radicals were formed and were captured by the iodine, proving that decarboxylation of the phenylvaleroxy radicals is not very fast compared to the rate of capture by iodine. Previous work, however, had shown that several products that arose from the phenylbutyl radical must have been formed in "cage" reactions (45). Since it is quite implausible that the iodine-capture reaction could be nearly as fast as a cage reaction, it follows that the decarboxylation of phenylvaleroxy radicals must be quite slow compared to cage reactions and hence that the large numbers of phenylbutyl radicals that participate in cage reactions must be primary decomposition products.

Supplementing the advances in our knowledge of the mechanisms of spontaneous decomposition of peroxides, Denney & Feig have contributed to the understanding of the induced decomposition reaction (46). They have shown that in the decomposition of benzoyl peroxide in diethyl ether, which is known to proceed practically entirely by the induced mechanism with the following chain-propagation steps,

$$C_6H_5CO_2\cdot + (C_2H_5)_2O \rightarrow C_6H_5CO_2H + CH_3\dot{C}HOC_2H_5$$

$$CH_3\dot{C}HOC_2H_5 + (C_6H_5CO_2)_2 \rightarrow C_6H_5CO_2\cdot + C_6H_5CO_2CH(CH_3)OC_2H_5,$$

the attack of the α-ethoxyethyl radical on benzoyl peroxide occurs predominantly at the peroxide oxygen rather than the carbonyl oxygen atoms. The decomposition in ether of benzoyl peroxide, labeled with oxygen-18 in the carbonyl group, gave α-ethoxyethyl benzoate that could be reduced by lithium aluminum hydride to benzyl alcohol containing 80 per cent of the original concentration of excess oxygen-18 used in the labeling. The peroxy oxygen is, of course, also the point of attack by various nucleophilic reagents (47, 48).

Solvent effects on radical reactions.—Russell's study of solvent effects on

radical halogenation reactions has now been published in detail (49). The tertiary hydrogen atoms of 2,3-dimethylbutane are only 4.2 times as reactive (per hydrogen) as the primary hydrogens at 25° and 3.7 times as reactive at 55° when the chlorination (photochemical) is carried out in the pure hydrocarbon. The addition of 4 M carbon tetrachloride, nitromethane, n-butyric acid, cyclohexene, trichloroethylene, propionitrile, dimethylsulfolane, isobutyronitrile, or silicon tetrachloride does not change this ratio by as much as 10 per cent, but aromatic and certain non-aromatic compounds are capable of increasing the selectivity of the chlorination. The following reactivity ratios were obtained with the solvents indicated (all at concentrations of 4 M and at 55°): nitrobenzene 4.9, benzotrifluoride 6.9, chlorobenzene 10.2, thiophene 13.3, benzene 14.6, anisole 18.4, mesitylene 25, and iodobenzene 31. At 25°, 4 M carbon disulfide gave a ratio of 33, and in 12 M concentration a value of 225. From the nature of the solvents that have no effect it is clear that the phenomenon is not a function of the dielectric constant or ion-solvating power of the medium, as are many solvent effects. Instead it appears that these increases in selectivity arise from the formation of complexes between the intermediate chlorine atom and the participating solvents. The complexed chlorine atom is much less reactive than a free chlorine atom, its hydrogen abstractions are undoubtedly endothermic, and therefore it is more selective. The selectivity would be expected to increase with the stability of the complex. This, coupled with the fact that the chlorine atom must be a quite strongly electron-attracting species, explains the tendency of electron-donating groups on the aromatic solvents to increase the selectivity. The selectivities were found to be well correlated with the basicities of the aromatic species as measured by their pi-complex formation with hydrogen chloride or by the (summed) *meta* σ constants of their substituents. Russell states that complexing is effective at increasing the difference in ease of abstraction of hydrogen atoms when that difference is due to a difference in the stabilities of the radicals being formed, but not when it is due to polar factors. Walling & Mayahi and den Hertog & Smit, on the other hand, state that differences of polar origin can also be modified by complexes (50, 51). Although it appears that polar effects are not, in general, as subject to variation by complexing as are radical stability effects, this subject would benefit from further investigation.

Stereochemistry of free radicals.—Recent studies on the stereochemistry of non-resonance-stabilized free radicals confirm current views on the subject and add detail in places, but no very convincing evidence has yet appeared that answers the question as to whether the most stable configuration of such radicals is planar or pyramidal. Kooyman & Vegter have studied the halogenation of norbornane using a number of halogenating agents (52). In all cases the attack on norbornane gave 2-norbornyl radicals almost exclusively. Chlorine and bromine gave about 70 per cent of the *exo*- and 20 to 25 per cent of the *endo*-2-norbornyl halides. The greater yield of the *exo* derivative is presumably due to the larger amount of space available near the methylene bridge, a conclusion that is strengthened by the observation that with the

bulkier reagents, sulfuryl chloride, phosphorus pentachloride, and carbon tetrachloride, about 95 per cent of the *exo* halide is obtained. With chlorine, phosphorus pentachloride, and sulfuryl chloride, where it is reasonable to presume that it is the highly reactive chlorine atom that attacks the hydrocarbon, a small amount of 7-norbornyl chloride is obtained, but in no case was any evidence found for the formation of 1-norbornyl chloride. The difficulty of abstracting hydrogen atoms from the bridgehead and the methylene bridge is understandable in view of the strained C—C—C bond angles at these positions since previous work on bicyclic and other relevant compounds has provided evidence that the optimum bond angles for a radical are more than 109.5°. On this basis, however, it might be expected that the hydrogens in the ethylene bridges of norbornane would also be deactivated, although to a lesser extent. Yet Kooyman & Vegter found these hydrogen atoms to have a reactivity comparable to those in cyclohexane.

The details of Goering & Larsen's report of stereospecific *trans* addition of hydrogen bromide and deuterium bromide to the 2-bromo-2-butenes have now been published (53). It appears that the 2,3-dibromo-2-butyl radical formed by the addition of a bromine atom to a 2-bromo-2-butene molecule abstracts a hydrogen atom from a hydrogen bromide molecule faster than it undergoes rotation around the central carbon—carbon single bond. This is possible at dry-ice temperatures where most of the reactants are in the liquid phase. At higher temperatures the addition reaction becomes more random, presumably because in the gas phase the intermediate radicals have a much greater average life time. It is difficult to check this explanation directly, however, because at higher temperatures *cis-trans* isomerization of the unreacted starting material begins to become significant. Skell & Allen have found that hydrogen and deuterium bromide also add cleanly *trans* to the 2-butenes (54).

Racemic products have been found in the N-bromosuccinimide bromination of (−)-α-deuterioethylbenzene (55), the peroxide- and photochemical transformations of active 2-octanesulfonyl chloride to 2-octyl chloride (56), and the photolysis of active 2-methylbutanal in the presence of iodine (yielding 2-butyl iodide) (57).

POLAR REACTIONS

Linear free energy relationships.—A number of rather general papers concerning linear free energy relationships have appeared recently. Benson has pointed out that the proper general method of correcting for the statistical factor is to divide the rate or equilibrium constant by K_σ, the ratio of the symmetry number for the reactants to the symmetry number for the products (58).

With the broad use of the older linear free energy relationships and the proliferation of new ones it is not surprising that attention has been given to the problem of the simultaneous operation of two such relationships. Wilputte-Steinert, Fierens & Hannaert have considered the simultaneous operation of the Hammett and the Grunwald-Winstein equations (59). Miller has

treated the simultaneous operation of two linear free energy relations in general (60). Thus, for example, in the case of the Hammett and Grunwald-Winstein equations the relation has the form

$$\log (k/k_o) = \rho_o\sigma + q\sigma Y + m_oY;$$

where k is the rate constant for the compound whose substituent constant is σ in the solvent whose ionizing power is Y, k_o is that for the unsubstituted compound in the reference solvent for which Y is defined as zero, ρ_o is the value of ρ in this solvent, m_o is the value of m for the unsubstituted reactant, and q is the rate of change of ρ with respect to Y (or equivalently, the rate of change of m with respect to σ). With a knowledge of ρ_o, q, m_o, and k_o (obtainable from the determination of four k's) for a given type of reactant, say α-phenylethyl chlorides, it would be possible to calculate the rate of solvolysis of any *meta*- or *para*-substituted α-phenylethyl chloride (if the appropriate σ constant is known) in any solvent whose Y value is known. Thus if 100 σ values and 40 Y values are known, this equation permits the calculation of all 4000 k values from a knowledge of only four parameters. Use of the Hammett equation alone would require 80 parameters and the Grunwald-Winstein equation would require 200. The reliability of the equation is, of course, no greater than that of the simpler equations from which it stems.

It has been shown that within the limits of applicability of the Hammett equation, or even a somewhat more general relationship in which, for every reaction two ρ's are permitted, one for the *meta*- and one for the *para*-substituted compounds, the ρ constant for any equilibrium is proportional to the difference in the σ constants of the groups being equilibrated (61). Thus for the equilibrium

$$ArX \rightleftharpoons ArY$$

involving *para*-substituted ArX's and ArY's,

$$\rho_p = \tau_p(\sigma_{p-X} - \sigma_{p-Y})$$

with an analogous expression being applicable to the *meta* compounds. The proportionality constants, τ_m and τ_p, are independent of the nature of the reaction and depend only on the reaction conditions (medium and temperature). It was further shown that if the Hammett equation held (in which ρ_p and ρ_m are identical), then the ratio

$$\tau_m/\tau_p = (\sigma_{p-X} - \sigma_{p-Y})/(\sigma_{m-X} - \sigma_{m-Y})$$

would be a constant for all X's and Y's. However, substitution of σ's derived from the defining reaction, the ionization of benzoic acids, shows that this ratio is not a constant. It therefore follows that the Hammett equation (with a unique value of σ for any given substituent) could not possibly be a general relation for all equilibria of *meta*- and *para*-substituted benzene derivatives.

Taft *et al*. (62, 63) have described a separate treatment of resonance effects made possible by the division of electronic effects in *meta*- and *para*-substituted benzene derivatives into resonance and inductive components

(64, 65). They find that the treatment used gives for neither m- nor p-substituents a correlation of resonance effects that is nearly as broadly applicable as the correlation of inductive effects reported earlier.

Charton has pointed out that the Hammett equation can be applied quite satisfactorily to the acidities of *trans*-3-substituted acrylic acids when the *para* σ constants are used (66, cf. 67).

Lewis, Suhr & Johnson have reported some extremes for the Hammett equation. The ρ constant for the equilibrium

$$ArN_2^+ + 2OH^- \rightleftharpoons ArN_2O^- + H_2O$$

(in no case was a detectable quantity of the intermediate species $ArN{=}NOH$ found) is 6.3, apparently the highest known (68). The σ constants for the diazonium cation group ($\sigma_m = 1.7$, $\sigma_p = 1.8 \pm 0.5$) and for phenols and aniline derivatives ($\sigma_p = 3$) also appear to be the highest yet observed (69).

Andrews & Keefer have described an interesting series of investigations on a rather unique group of compounds, the iodobenzene dichlorides (70, 71). Their measurements include one of the few available Hammett-equation treatments in which neither the reactants nor products are ionic species, and also comprise one of the few quantitative studies that have been made on a whole new family of substituents, such as $-SF_5$, $-CF_2SF_5$, $-SF_4CF_3$, etc., containing an atom with more than eight electrons in its outer shell because of the attachment of a large number of monovalent groups. Rate and equilibrium constants for the formation and dissociation of a number of substituted iodobenzene dichlorides were determined. Although neither the rate nor the equilibrium constants give a very good Hammett-equation correlation, the results show clearly that electron-donating substituents increase the rate constants for dissociation of the dichlorides slightly, increase the equilibrium constants for formation of the dichlorides more, and increase the formation-rate constants the most. From these results it follows that the $-ICl_2$ group is more electron-withdrawing than $-I$ and that the transition-state group is still more strongly electron-withdrawing. The iodobenzene dichlorides are more dissociated in acetic acid than in nitromethane and are still more dissociated in carbon tetrachloride, probably because they are more polar than the materials from which they are formed. The influence of most *ortho* groups on the equilibrium constants appears to be largely polar rather than steric, in agreement with the fact that the two chlorine atoms do not lie in the plane of the aromatic ring [in the crystalline state, at least (72)]. A number of *ortho* groups have a marked accelerating influence on the rate of establishment of the equilibrium, apparently because of neighboring group participation. In addition to the obvious cation-stability factor, which must be of importance in such participation, it appears that the formation of five-membered rings is favored over the formation of six-membered rings. Thus, the *ortho* groups $-CO_2H$, $-CO_2CH_3$, and $-CH_2OH$, which can form five-membered rings, greatly accelerate the rate, while the less basic group COCl does not. Although the rather similar groups $-OCOC_6H_5$ and

—OCOCH$_3$, which would have to form six-membered rings, do not give rate enhancement, the groups —NHCOC$_6$H$_5$ and —NHCOCH$_3$, which may participate to give cations with the positive charge on nitrogen, do speed the reaction. The neighboring-group explanation of the accelerating influence of the substituents mentioned is supported by the isolation of the compound 1 from the dichloride of *o*-iodobenzoic acid.

1.
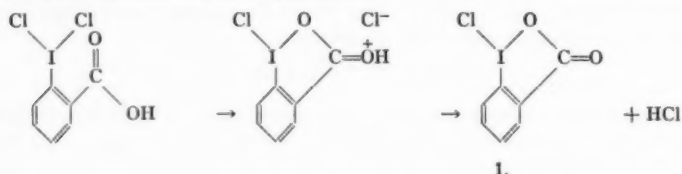
Aromatic rearrangements.—Spryskov & Erykalov have found that the equilibrium mixture of dichlorobenzenes produced by heating any of the isomers with aluminum chloride at 160° contains about 17 per cent *ortho*, 53 per cent *meta*, and 30 per cent *para* isomer (73). Although this reaction could be explained as a dechlorination-rechlorination, perhaps by a mechanism in which a proton is donated to a chlorine-bearing carbon atom to give an intermediate capable of donating a chloronium ion, this is shown to be improbable by the observation that very little disproportionation to chlorobenzene and trichlorobenzenes occurs. More compelling evidence is the fact that the isomerization of *p*-dichlorobenzene initially yields very little of the *ortho* isomer and vice versa. It thus appears that the isomerization is an internal rearrangement.
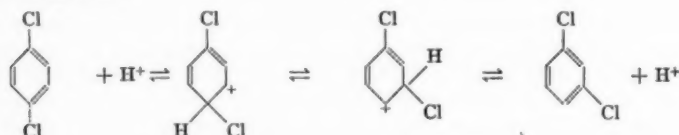
The reaction mechanism is thus probably analogous to the internal rearrangement of the xylenes (74).

By showing that there was no nitrogen-15 in either the *o*- or *p*-nitroaniline produced by the acidic rearrangement of N-nitroaniline in the presence of nitrogen-15 labeled nitric acid, Brownstein, Bunton & Hughes proved that even the *para* compound was formed by an internal rearrangement (75). Blackall *et al.* have found that the O-nitrations of methanol, *p*-nitrobenzyl alcohol, ethylene glycol, trimethylene glycol, and the primary oxygen of glycerol (76), and the N-nitrations of N-methyl-2,4,6-trinitroaniline and N-methyl-2,4-dinitroaniline (77) by about 3.0 M nitric acid (a large excess) in nitromethane are all zero-order reactions. Since the rate constants and the effects of added nitrate ion, water, etc. are the same as previously observed in the nitration of aromatic hydrocarbons there is little doubt that

the rate-controlling step of the reaction is the formation of the nitronium ion.

Carbonium ions.—A striking confirmation, by direct measurement, of the existence of an intermediate already established by indirect measurements, was found in Rosenbaum & Symons' spectroscopic detection of *t*-butyl cations in sulfuric acid solutions of *t*-butyl alcohol or isobutylene (78).

Also detected directly was a much more surprising organic cation, a carbonium ion bearing two positive charges. Hart & Fish noted that trichloromethylpentamethylbenzene dissolves readily in 100 per cent sulfuric acid to give a red solution with a van't Hoff *i*-factor of five (79). With the added observation that bubbling nitrogen through the solution removed two moles of hydrogen chloride, reduced the *i*-factor to three, and gave a solution that liberated, upon the addition of water, one mole each of pentamethylbenzoic and hydrochloric acids, the conclusion seems inescapable that the reaction proceeded as follows:
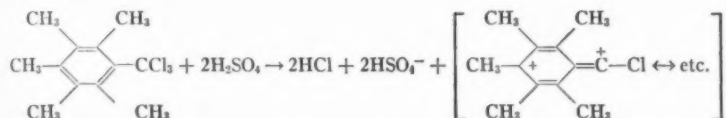
Leal & Pettit have reported measurements on a non-classical carbonium ion (80). The alcohol 2 or the diene 3, in which the five- and six-membered rings are fused *cis*, dissolved in sulfuric acid to give a yellow solution with an absorption maximum at 427 mμ,
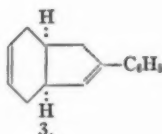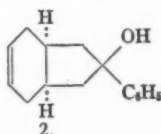
whereas the isomer whose rings were fused *trans* gave a sulfuric acid solution that did not absorb above 300 mμ. Apparently the double bond in the six-membered ring is involved in the stabilization of the positive charge located in the other ring. It was further found that the chloride corresponding to the alcohol 2, upon reaction with silver perchlorate, gave a yellow solid that was insoluble in hexane, chloroform, carbon tetrachloride, and benzene. This salt dissolved in nitromethane to give a rather unstable solution whose spectrum is much like that of 2 or 3 in sulfuric acid; it reacted with water to give the diene 3.

Bartlett and co-workers have found that the intermediate carbonium ion in the acid-catalyzed rearrangement of 2-*p*-anisylcamphenilol is a relatively stable, long-lived species upon which direct spectral measurements can be made (81).

Doering and co-workers have isolated a salt of the heptamethylbenzenon-

ium ion 5 as a product of the exhaustive aluminum-chloride catalyzed methylation of methylbenzenes (82, cf. 83). In aqueous solution, this salt is transformed to the hydrocarbon 4-methylene-1,1,2,3,5,6-hexamethylcyclohexadiene-2,5, compound 4.

4.

5.
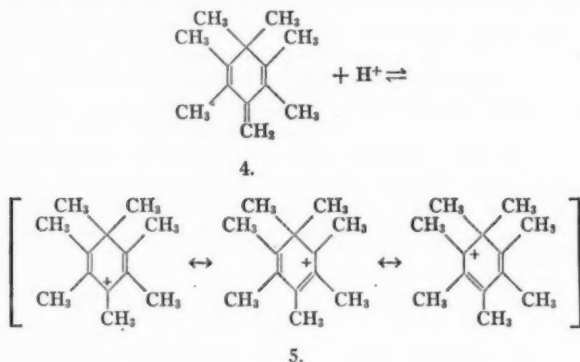
The stability of the carbonium ion 5, relative to the hydrocarbon, is so great that the latter dissolves in 4 N or stronger hydrochloric acid to give solutions of the carbonium ion's salt. Upon standing for several weeks, aqueous solutions containing the cation 5 yield methanol and hexamethylbenzene, no doubt by S_N2 attack of water on one of the two methyl groups attached to the same-carbon atom.

Streitwieser & Coverdale have found that the reaction of *cis*-cyclohexylamine-2-*d* with nitrous acid gives *cis*-cyclohexanol-2-*d* with at least 94 per cent retention of configuration (84). These results suggest that the intermediate cyclohexyl carbonium ions react with the solvent molecules faster than they undergo conformational change.

Grob and co-workers have found that bicyclo[2,2,2]-2,5-octadiene gives both normal and homoallyllic addition with bromine but only normal addition with perbenzoic acid and 2,4-dinitrobenzenesulfenyl chloride (85, 86).

Nucleophilic displacements on carbon.—Proofs of various organic reaction mechanisms continue to be published in spite of such opinions as, "Published statements to the effect that a given mechanism has been proven are evidence chiefly of the scientific immaturity of the writer and of the laxity of the editor" (87). If the word "proven" in this quotation is used in the sense of the mathematician or logician, then it would seem better to replace the word "mechanism" by "theory or law of experimental science" so as to avoid the implication that the unreliability of reaction mechanisms places them in a class apart from other scientific concepts. Such a restriction in the meaning of the term might virtually exclude it from use in the discussion of scientific theories and may be unattainable at this late date. The term will

be used here in the broader sense often employed by experimental scientists.

Considering the high degree of probability already established for the two-step mechanism for activated nucleophilic substitution on aromatic rings and the strong new supporting data of Bunnett & Randall, it seems reasonable to consider the two-step (at least) character of the reaction as proven (88). Bunnett & Randall found that the reaction of N-methylaniline with 2,4-dinitrofluorobenzene was general base-catalyzed. The rate in ethanol containing potassium acetate, for example, increased linearly with the potassium acetate concentration. They point out that this base-catalysis can be explained by the following mechanism:

$$ArX + PhNHMe \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar\overset{\overset{\displaystyle Ph}{\overset{\displaystyle |}{\underset{\displaystyle |}{\overset{+}{N}HMe}}}}{\underset{\displaystyle X}{\diagdown}} \overset{k_2}{\rightarrow} Ar\overset{Me}{\overset{|}{N}}-Ph + HX$$

6.

$$k_3 \downarrow base$$

$$Ar\overset{\overset{\displaystyle Ph}{\overset{\displaystyle |}{\underset{\displaystyle |}{N-Me}}}}{\underset{\displaystyle X}{\diagdown}} \rightarrow Ar-\overset{Me}{\overset{|}{N}}-Ph + X^-$$

7.
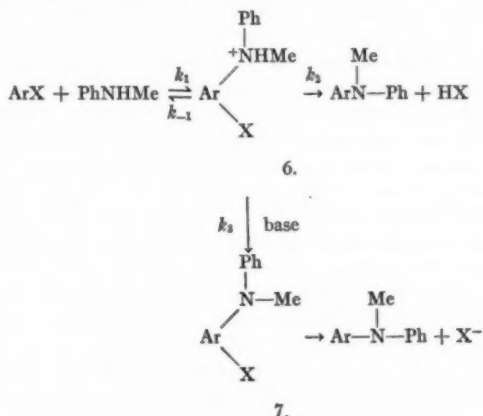
in which the function of the base is to dehydrohalogenate the reactive intermediate 6, probably via the deprotonated intermediate 7. While the observation of potassium acetate catalysis could be explained by the transformation of a small amount of N-methylaniline to its more reactive conjugate base in a rapid equilibrium process (a rate-controlling reaction of acetate ion with N-methylaniline would give an overall reaction rate independent of the aromatic halide concentration instead of first order in aromatic halide as observed), this explanation was disposed of by the observation that the potassium-acetate catalyzed reaction was not slowed by the addition of acetic acid. The reaction was also shown to be catalyzed by hydroxide ion in aqueous dioxane in a manner that was said to become somewhat less than linear at higher hydroxide ion concentrations as the reaction step governed by k_3 becomes comparable in rate to that governed by k_{-1}. This point does not appear to have been as firmly established by the experimental results, whose interpretation is complicated by the competing direct reaction of the hydroxide catalyst, a reaction that in some instances proceeded more than 100 times as fast as the reaction whose catalysis was being

investigated. The analogous reactions of 2,4-dinitrochlorobenzene and 2,4-dinitrobromobenzene are not subject to general base catalysis, presumably because the intermediates in these cases decompose to product much more rapidly than they revert to reactant. The decomposition of these intermediates is said to proceed by the step governed by k_2, whose mechanism is not given explicitly but is implied to involve the initial loss of X as an anion (the proton transfer governed by k_3 would not be expected to be much faster than in the case of the fluoride, although a concerted dehydrohalogenation would be). One unusual (but not impossible) aspect of the reaction mechanism should be noted. The loss of a proton from the fairly highly acidic ammonium ion 6, even in the presence of appreciable concentrations of acetate or hydroxide ion, is said to be slower than the cleavage of a carbon—nitrogen bond. The studies by Ross and co-workers of the reactions of 2,4-dinitrochlorobenzene with amines also support the two-step mechanism (89 to 91).

Green & Hudson have found that the sequence of reactivities of a number of nucleophilic reagents toward ethyl chloroformate is much different from the sequence found for typical nucleophilic displacements at saturated carbon (92). They found: $(CH_3)_2CNO^- \gg OH^- > C_6H_5O^- > NO_2^- > N_3^- > F^- > S_2O_3^{--}$, Cl^-, Br^-, I^-, OCN^-, SCN^-, ClO_3^-, and NO_3^-, noting that only ions derived from first-row elements were highly reactive and that the acetoxime and phenoxide anions were more nucleophilic than might be expected from comparison with the hydroxide ion. It is of interest that Ingold has suggested that the sequence of nucleophilicities toward saturated carbon may not apply to the case of carbonyl carbon (93).

Additional studies of internal catalysis by imidazole groups have been described. The hydrolysis rate of n-propyl γ-(4-imidazolyl)-thiobutyrate shows that strong internal nucleophilic participation is occurring (94). Bruice & Sturtevant found that the amide and phenyl esters and probably the methyl ester of γ-(4-imidazolyl)-butyric acid undergo hydrolysis via participation by the imidazole group (95). The p-nitrophenyl ester hydrolyzed at practically the same rate as that observed previously for the α-chymotrypsin-p-nitrophenyl acetate complex (96), showing that in this case simple monofunctional internal catalysis can explain the high rates at which enzymes can bring about reactions of substrates with which they have coordinated. More work with model systems on the mechanism of coordination would be worthwhile, although advances are being made in this area, too.

The formation of ethylene oxide from ethylene chlorohydrin and sodium hydroxide at 25° has been found by two groups of workers to go 54 per cent faster in D_2O than in H_2O (97, 98). This shows that the reaction is not concerted but involves the reversible intermediate formation of the 2-chloroethoxide ion, which occurs to a greater extent in D_2O.

Nucleophilic displacements on atoms other than carbon.—A steadily mounting tide of interest may be noted in studies of reactivity and reac-

tion mechanisms of nucleophilic displacements at elements other than carbon, including particularly the hydrolysis of esters of inorganic acids. Bunton, de la Mare and co-workers have described some of the results of their studies on the hydrolysis of sulfites (99 to 102). With ethylene, propylene, *meso*-2,3-butylene, tetramethylethylene, trimethylene, and 1,3-butylene sulfites, the use of oxygen-18 showed that cleavage occurred at the sulfur-oxygen bond in both acidic and basic solutions (99). Sulfur-oxygen bond cleavage was also established for the acidic hydrolysis of diethyl and dimethyl sulfites (102). For ethylene and trimethylene sulfites, it was observed that the unreacted ester recovered from a partially completed hydrolysis in oxygen-18 enriched water contained no excess oxygen-18 (99). Because of possible driving forces for preferential ring-opening in an "orthosulfite-type" intermediate, it would be of interest to learn the result of similar experiments on such acyclic sulfites as the diethyl and dimethyl esters. The basic hydrolysis of the sulfites that contained six-membered rings was slower than that of the five-membered ring compounds, which were too reactive to study conveniently by the usual techniques. The rates of the acid hydrolysis of the cyclic compounds did not differ greatly but all of them were considerably less reactive than diethyl or dimethyl sulfite. Considerable effort was expended in an investigation of the relation between the reaction rate and h_o or the acid concentrations. As in the case of a great many such studies the results appear to be inconclusive.

Sommer and co-workers have made some quite significant studies on the stereochemistry of nucleophilic displacement reactions on silicon. They have determined the rate constants for the displacement of hydride ion from the silicon atom in 1-methyl-1-silacyclobutane 8, 1-silabicyclo[2,2,1]heptane 9, and 1-silabicyclo[2,2,2]octane 10 (103, 104).

CH₂—CH₂
│   │
CH₂—Si—CH₃
      │
      H

8.

CH
CH₂   CH₂
│ CH₂ │
CH₂   CH₂
      Si
      │
      H

9.

CH
CH₂ CH₂ CH₂
│   │   │
CH₂ CH₂ CH₂
      Si
      │
      H
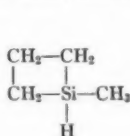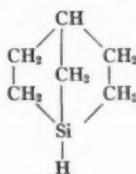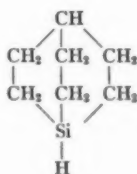
10.

Compound 8 was 10^4 to 10^5 times as reactive, 9 was 10^3 times as reactive and 10 was 10 times as reactive as the acyclic compound triethylsilane. This correlation of reactivity with the extent to which the silicon valence bonds are distorted is strong evidence that during the reaction the silicon atom acquires an sp^3d configuration with the entering and departing groups attached to one axial valence bond and one equatorial valence bond of the triangular bipyramid around silicon. Although the reactions of the bicyclic compounds must give retention of configuration, Sommer & Frye have shown that dis-

placements on silicon can also be carried out with pure inversion of configuration (105).

Electrophilic displacements on carbon.—While the electrophilic displacement of mercury from carbon is also a nucleophilic displacement on mercury, most of the interest in such reactions has been in the behavior of the carbon atom. Support continues to mount for the belief that in such reactions retention of configuration at carbon is strongly favored even when the attacking electrophilic reagent has no nucleophile attached to it capable of keeping it strongly coordinated to the mercury atom being displaced. Charman, Hughes & Ingold have found that the kinetically second-order reaction of optically active di-*sec.*-butyl mercury with mercury salts proceeds with retention of configuration (106). The reaction rate increased strongly in the order $LiHgBr_3 < HgBr_2 < Hg(OAc)_2 < Hg(NO_3)_2$. This order of reactivities was said to prove that the reactions were S_E2 rather than S_Ei in character. It might be more conservative to state that if the reactions are of the S_Ei type, it is apparent that the formation of the new carbon-mercury bond is of more importance than the formation of a new bond to the mercury atom being displaced.

The studies of Cram and co-workers on methods of changing the stereochemical results of such reactions as

$$\overset{*}{\underset{/}{\diagdown}}C \overset{\frown}{\underset{\smile}{}} X \overset{\frown}{\underset{\smile}{}} Y + H{-}B \rightarrow \overset{*}{\underset{/}{\diagdown}}C\,{-}H + \dot{X}{=}Y + \bar{B}$$
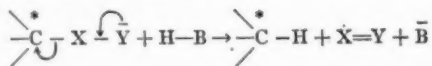
from predominant retention to predominant inversion, largely by changes in the concentration and nature of the proton donor HB, have now been published in detail (107 to 113).

Stiles & Finkbeiner have utilized the driving force provided by chelation of the product in devising methods for the carboxylation of aliphatic nitro compounds and ketones (114, 115). The reactions of magnesium methyl carbonate with primary nitro compounds and ketones of the type RCH_2COR were found to give the chelated magnesium salts of the α-nitroacids and β-ketoacids, respectively.

Carbonyl addition reactions.—The question of whether the reactions of carbonyl compounds with hydroxylamine and hydrazine derivatives ordinarily involve rapid reaction of the carbonyl compound with acid followed by rate-controlling combination with RNH_2, or rapid reversible association of RNH_2 and the carbonyl compound followed by a rate-controlling dehydration by acid (116), has been resolved in favor of the latter alternative by Jencks' careful and penetrating investigation (117). Jencks showed that the ultraviolet carbonyl absorption of representative aldehydes and ketones was markedly diminished almost instantaneously by the addition of hydroxylamine, methoxyamine, hydrazine, or semicarbazide at concentrations of several tenths molar and pH's near neutrality. From the extent of the decrease in absorption, the equilibrium constant for the formation of the addition

compound 11 was determined. The rate of formation of the oxime or hydrazone derivative at pH's between 4.6 and 7.6, as measured by the increase in the initially diminished ultraviolet absorption, was proportional to the product of the hydrogen-ion concentration and the fraction of the carbonyl compound present as its addition compound. Experiments at varied buffer concentrations showed that the reaction was also subject to general acid catalysis. The abbreviated mechanism,

$$\diagup \hspace{-0.3em}\diagdown C=O + H_2NOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad \diagup \hspace{-0.3em}\diagdown C \begin{smallmatrix} O-H \\ : \\ : \\ N-O-H \\ | \\ H \end{smallmatrix} \quad \overset{H^+}{\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}} \quad \diagup \hspace{-0.3em}\diagdown C=NOH + H_2O$$
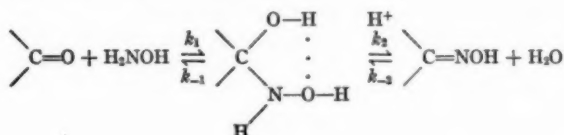
11.

with the acid-catalyzed dehydration step governed by k_2 being rate-controlling, explains these observations. The rate maximum near pH 4, often reported for reactions of this type, is apparently not due to general acid catalysis as believed earlier (116). Changing the pH of the reaction solution from 8 or 9 to a lower value initially increases the reaction rate because of the increase in the rate of the dehydration step; around pH 4 the rate levels off because of a compensating transformation of RNH_2 into its unreactive conjugate acid; in more acidic solutions the rate falls as the addition of the increasingly scarce, free RNH_2 base to the carbonyl compound becomes the rate-controlling step. In a still more acidic solution the rate levels off again as the carbonyl compound begins to react in the form of its conjugate acid whose increasing concentration compensates for the decreasing concentration of free base. The rate-increase observed in oximation in basic solution is believed due to the incursion of a base-catalyzed dehydration. In order to explain the fact that such bases as piperidine and imidazole gave no evidence for the formation of addition compounds to the aldehydes and ketones studied, it seemed necessary to postulate the stabilization of the adduct by hydrogen-bonding as shown for the hydroxylamine adduct 11, although steric factors may also be important. Hydrazine seems to have formed a less stable complex than might have been expected from the hydrogen-bonding explanation.

The difference in orientation in acid- and base-catalyzed aldol condensations of unsymmetrical ketones has been studied by two groups of workers who reached essentially the same conclusions. Stiles, Wolf & Hudson found that the treatment with base of either of the hydroxyketones, 12 or 13, gave the same α,β-unsaturated ketone 14, showing that the reversal of the aldol condensation is, in the case of 13, faster than the dehydration reaction. Even with 12, the formation of benzaldehyde in the reaction with base showed that the reverse aldol is comparable in rate with the dehydration (118).

$$C_6H_5CH\!-\!CH_2COC_2H_5 \;+\; OH^- \;\rightarrow\; C_6H_5CH\!-\!\overset{-}{C}HCOC_2H_5$$
$$\underset{OH}{|} \;\Updownarrow\; 12.$$
$$C_6H_5CH\!-\!CH_2COC_2H_5 \qquad\qquad \underset{OH}{|} \;\downarrow$$
$$\underset{O^-}{|} \;\Updownarrow\; {}^- \qquad\qquad C_6H_5CH\!=\!CHCOC_2H_5 + OH^-$$
$$C_6H_5CHO + \overset{-}{C}H_2COC_2H_5 \rightleftharpoons \qquad\qquad\qquad 14.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad CH_3COC_2H_5 + OH^-$$
$$C_6H_5CHO + CH_3CO\overset{-}{C}HCH_3 \rightleftharpoons$$
$$C_6H_5CH\!-\!\overset{|}{C}HCOCH_3 \;\rightleftharpoons\; C_6H_5CH\!-\!CHCOCH_3 + OH^-$$
$$\underset{O^-}{|}\;\;\underset{CH_3}{|} \qquad\qquad \underset{OH}{|}\;\;\underset{CH_3}{|}$$
$$13.$$
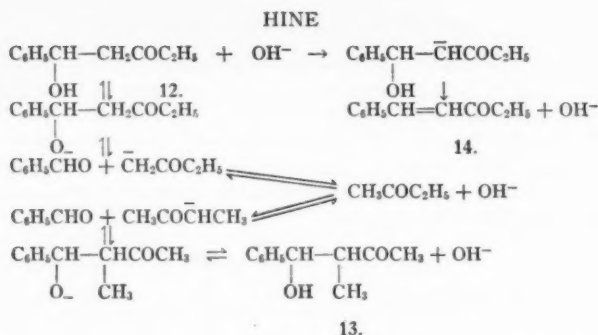
Thus, the rate of formation of 14, the only product found in the base-catalyzed condensation of benzaldehyde with methyl ethyl ketone, is controlled by the rate of dehydration of the intermediate β-hydroxyketone. The probable greater difficulty of dehydration of 13 compared to 12 may be due to a greater acidity of the α-hydrogen atoms of 12, a factor that could be of importance even if the dehydration is concerted instead of stepwise as shown. (Stiles, Wolf & Hudson did not commit themselves as to the mechanism of the dehydration step.) In acid solution, both 12 and 13 undergo simple dehydration without carbon-skeleton rearrangement. Therefore, the fact that the branched-chain product $CH_3COC(CH_3)\!=\!CHC_6H_5$ is formed essentially exclusively in the acid-catalyzed reaction of benzaldehyde and methyl ethyl ketone shows that under these conditions the hydroxyketone 12 is never formed. That is, the rate-controlling step of the reaction occurs before the dehydration and must be the addition of the protonated aldehyde to the enol form of the ketone since the reaction rate is dependent on the aldehyde, ketone, and acid concentrations. Noyce & Reed have come to the same conclusions from a somewhat different approach (119).

Acids and bases.—Cohen, Lacher & Park have prepared the interesting new compound, diketocyclobutenediol, whose pK_1 is about 1.0 and whose pK_2 is 2.2 (120).

Rapoport & Smolinsky have prepared fluoradene (pK *ca.* 11), which appears to be the most acidic hydrocarbon known (121).

fluoradene
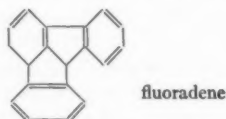
Values of H_o have been determined in the systems sulfuric acid-methyl isobutyl ketone (122), 20 per cent ethanol—80 per cent sulfuric acid-water (123), trifluoroacetic acid-hydrogen fluoride and trifluoroacetic acid-sulfuric acid (124), and aqueous solutions of methanesulfonic, sulfuric, phosphoric, formic, trichloroacetic, and acetic acids (125). Values of H_R (also known as

J_o and C_o) have been reported for aqueous perchloric and nitric acid solutions (126).

Medium effects.—Various investigators have occasionally wondered whether micelle formation had any significant effects on reaction rates. Duynstee & Grunwald have now shown clearly that such effects may be quite important (127). Thus the rate of alkaline fading of crystal violet, in which the tris(dimethylaminophenyl)methyl cation (*ca.* 10^{-5} *M*) combines with a hydroxide ion, is increased about fourteenfold by the presence of the cationic detergent salt cetyltrimethylammonium bromide and decreased by about the same factor by the anionic sodium lauryl sulfate, both at concentrations of 0.01 *M*. The large organic reactant ion is believed to be incorporated in the micelles that these detergents are known to form at the concentrations used. The rate effects are caused by the attraction of hydroxide ions to the cationic micelles and their repulsion by the anionic micelles.

The observations of Van Looy & Hammett that sulfuric acid appears to react with nitroanilines (NA) in nitromethane by the following processes (128)

$$H_2SO_4 + NA \rightleftharpoons HNA^+ \cdot HSO_4^-$$

and

$$3H_2SO_4 + NA \rightleftharpoons HNA^+ \cdot HSO_4(H_2SO_4)_2^-$$

should sound a warning to those who expect the same kind of behavior from all solvents that have a fairly high dielectric constant as is familiar for hydroxylic solvents.

METHYLENES

Etter, Skovronek & Skell have made a major contribution to the singlet-triplet question for methylenes in their study of diphenylmethylene (129). This intermediate (generated by the photolysis of diphenyldiazomethane) was found to add to *cis*- and *trans*-2-butenes in a nonstereospecific manner and to react with 1,3-butadiene and 1,1-diphenylethylene more than 100 times as rapidly as with 1-hexene, isobutylene, or cyclohexene, a reactivity sequence characteristic of radicals but not of the methylenes that have been studied to date. These observations show that diphenylmethylene is very probably a diradical (triplet). Furthermore, the proof that two types of chemical behavior are possible for methylenes strongly supports the classification of methylenes as singlets and triplets on the basis of this chemical behavior.

Skell & Starer have found striking rearrangements in the hydrocarbon products from the action of alkoxide ions on chloroform and bromoform (130). Isobutylene, 1-butene, *cis*- and *trans*-2-butenes, and methylcyclopropane were all formed in the reaction of the isobutoxide ion with bromoform in isobutyl alcohol solution. It therefore appears that the intermediate alkoxyhalomethylene (131) loses a halide ion to give the cation ROC$^+$ which, being isoelectronic with an alkyl diazonium ion, loses carbon monoxide to give a carbonium ion that rearranges.

$$RO^- + CCl_2 \rightarrow ROCCl + Cl^-$$

$$ROCCl \xrightarrow{-Cl^-} ROC^+ \rightarrow CO + R^+ \xrightarrow{\text{rearrangement}}$$
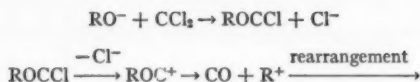
A number of new synthetic procedures for cyclopropane derivatives involving the action of strong bases on organic halides in the presence of olefins appear, with varying degrees of probability, to involve the intermediate formation of methylenes (132 to 138).

Shilov & Sabirova have described evidence that the vapor-phase pyrolysis of chloroform is initiated by a single-step transformation to hydrogen chloride and dichloromethylene (139).

Volpin, Dylova & Kursanov have reported that tropylium salts may be formed in yields of around 1 per cent by the action of potassium t-butoxide on methylene chloride in the presence of benzene (140). Chloromethylene was presumed to be a reaction intermediate.

Mechanism of the reaction of methylene with the C—H bond.—The transformation of the

$$\underset{/}{\overset{\backslash}{-}}C-H \text{ group to } \underset{/}{\overset{\backslash}{-}}C-CH_3$$
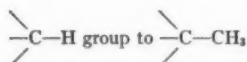
by the action of methylene has been found to proceed partly by a direct insertion mechanism and partly by a free radical process. Doering & Prinzbach studied the photolysis of CH_2N_2 in the presence of $(CH_3)_2C{=}C^{14}H_2$ in both the liquid and the gas phase (141). If the formation of 2-methyl-1-butene in this reaction proceeds via an intermediate methallyl radical, the product should have its carbon-14 equally distributed between the first and third carbon atoms.

$$CH_2 + (CH_3)_2C{=}C^{14}H_2 \rightarrow CH_3\cdot + \left[\begin{array}{c} CH_3 \\ | \\ \cdot CH_2-C{=}C^{14}H_2 \\ \updownarrow \\ CH_3 \\ | \\ CH_2{=}C-C^{14}H_2\cdot \end{array} \right]$$

$$CH_3C^{14}H_2C(CH_3){=}CH_2 \text{ and } \leftarrow$$
$$CH_3CH_2C(CH_3){=}C^{14}H_2$$
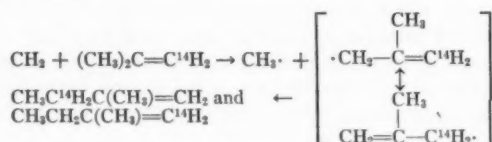
On the other hand, if the reaction involves the direct insertion of methylene between the carbon and hydrogen atoms being attacked, the resultant 2-methyl-1-butene should have all of its carbon-14 at the first carbon atom. The 2-methyl-1-butene isolated from the gas-phase reaction had 92 per cent of its carbon-14 at the first carbon atom, showing that 84 per cent of it was formed by the direct insertion mechanism and 16 per cent by the radical mechanism. This demonstrates that more than 16 per cent of the instances of methylene attack on the methyl groups of isobutylene resulted in radical formation, because the intermediate methallyl radicals could enter into other reactions such as dimerization and hydrogen abstraction (the unreacted isobutylene recovered from the reaction had had its carbon-14 rearranged slightly), besides combining with a methyl radical.

Frey has estimated the relative extent of occurrence of the radical- and direct-insertion mechanisms in the attack of methylene on propane (142). The formation of such products as n-hexane, 2-methylpentane, and 2,3-dimethylbutane established the intermediacy of n-propyl and isopropyl radicals. With a plausible assumption about the relative rate constants for the various radical-pairing reactions, it is stated that methylene abstracts secondary hydrogen seven times as rapidly as primary hydrogen, thus showing a selectivity comparable to that of the methyl radical. From the relative yields of the various products it is estimated that around 78 per cent of the initial attack is by direct insertion and 22 per cent by hydrogen abstraction.

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RADIATION CHEMISTRY[1]

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Recent reviews include the following: a survey of publications during 1958 by Charlesby & Swallow (1); a general survey of gases, aqueous solutions, and hydrocarbons by Henglein (2, 3), and a survey of elementary processes by Burton, Hamill & Magee (4). Also of general interest are the Lind Jubilee issues (June, 1959) of the *Journal of Physical Chemistry, Radiation Research*, and the *Journal of Chemical Education*. The proceedings of the Moscow Conference, 1957, have appeared in English translation (5) as have those of the Geneva Conference, 1958 (6). Organic peroxides in radiobiology have been considered in Volume 4 of a series on the chemical and biological effects of radiation, under the editorship of Haissinsky. It includes papers by Douzou, M. Durup, J. Durup, Okada, Vermeil, and Weiss (7). A book on radiation biology includes a chapter by Platzman on the physical and chemical basis of mechanisms (8). The behavior of various materials under radiation is reviewed in a book that includes chapters on organic substances by Burton and on polymers by Charlesby (9). A published series of lectures emphasizes the practical applications of radiation chemistry (10). The collected papers of the *Joint Conference on Mass Spectrometry* held in London, September 24–26, 1958, were published (11). Also of interest are *Principles of Radiation Dosimetry* by Whyte (12) and the proceedings of an informal discussion on the radiation chemistry of water at the University of Notre Dame (13).

A new journal on radiation biology, including related studies in physics and chemistry, has appeared (14). The first Miller conference was held April 20–24, 1959, in Wales; the Faraday Society held an informal discussion on *The Chemical Effects of Radiations on Nucleic Acids and Other High Polymers* simultaneously with the first meeting of the newly formed Association for Radiation Research at King's College, Newcastle-upon-Tyne, March 23–25, 1959.

GASES

Electron impact.—Lassettre has reviewed parts of his unpublished work dealing with collision cross sections for electron scattering by molecular gases and has compared excitation by electron impact and by optical absorption, particularly for oxygen and water (15). Gaseous ion-molecule reactions were reviewed by Hamill (16).

Electron impact measurements are making important contributions to

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radiation chemistry. They include data for unimolecular and bimolecular ion kinetics, electron attachment cross sections, and energetics, as well as the relatively familiar thermochemical data for positive ions and free radicals. Although the ease of measurement has produced abundant information, reliability of appearance potentials is ordinarily not better than ± 0.1 ev. After critically comparing various methods, however, Nicholson (17) concluded that Morrison's second differential method (18, 19) for measuring ionization potentials by electron impact is accurate within ± 0.02 ev. Chupka has critically considered the effects of predissociation and initial internal energy on the appearance potentials of polyatomic molecules. He found very small kinetic energies of fragment ions from n-propylamine, n-propanol, and methyl ethyl ketone. Although the quasi-equilibrium theory of Rosenstock et $al.$ (20) is qualitatively correct for the processes observed, it is quantitatively inadequate near the threshold region. In terms of the theory, experiments are consistent with a much smaller number of oscillators (21). Reaction mechanisms to account for the observed mass spectra of normal and labeled methyl formate, methyl acetate, and ethyl formate have been proposed by King & Long (22). Again the quasi-equilibrium theory can account for the results with 70 v. ionizing electrons but is inadequate at lower energies. Another difficulty encountered in experimental tests of the theory of unimolecular decomposition is that ions R^+ from RH do not appear with the expected abundance from propane and lower aliphatic alcohols. Friedman, Long & Wolfsberg (23) have extended earlier work to the C_4—C_8 alkanes at low ionizing voltages with a similar observation. For n-pentane, frequency factor ratios $1:10^4:10^8$ must be assigned to account for $H:CH_3:C_2H_5$ elimination. These results indicate oversimplification of the applied theory. Stevenson (24) has compared the average excitation energy for molecular ions formed by electron impact, as determined by the quasi-equilibrium rate theory, with results deducible from mass spectrometric appearance potentials. The good agreement supports the applicability of the theory to mass spectra and hence to radiation chemistry. Ion-molecule reactions are much faster than neutralization but, according to calculations, dissociations of some types of molecule ions (e.g., CH_4, C_2H_4, C_6H_6) may be slower than collisional deactivation in the atmospheric gas. For more complex alkanes, rates of dissociation of molecule-ions are comparable with ion-molecule reaction rates and reactions of fragment ions become important. According to Coggeshall (25) the mass spectral patterns of n-paraffins do not correspond to predictions based upon a postulated relation with net positive charge distribution from an extension of the Lennard-Jones and Hall theory (26).

The retarding potential-difference method of Fox et $al.$ (27) has been used repeatedly to obtain appearance potentials of both positive and negative ions by essentially monoenergetic electrons. Using this technique, Hickham & Fox (28) showed that SF_6^- forms by resonance electron capture. This accurate determination makes it possible to employ SF_6 as a convenient

internal standard for measuring negative ion appearance potentials and the energy width for electron capture. Hickham & Berg (29) used this method with a conventional electron gun to investigate negative ions from several halogenated methanes and ethanes. The probability for electron attachment by SF_6 and CCl_4 showed marked temperature dependence. Biondi & Fox (30) determined the cross section for dissociative attachment of electrons by iodine; the maximum value at zero energy is $30A^2$. Since values of cross sections for electron attachment by molecules are quite scarce, the following measurements by Buchel'nikova (31), with electron energies at maximum ion currents, are of interest: $0.78A^2$ at 0.05 ev for I^- and $0.32A^2$ at 0.9 ev for F^- from CF_3I; $0.28A^2$ at 0.4 ev for Cl^- from BCl_3; $0.04A^2$ at 0.6 ev and $0.06A^2$ at 0.5 ev for X^- from HCl and HBr; $1.36A^2$ at 0.02 ev for Cl^- and $1.0A^2$ at 0.6 ev for CCl_4^- (tentative); $0.01A^2$ at 8.6 ev for H_2O^- (tentative); $5.7A^2$ at 0 ev for SF_6^-. Buchel'nikova also reported $12 \pm 4A^2$ at 0 ± 0.01 ev for SF_6^- (32). Frost & McDowell (33a) found appearance potentials for resonance electron attachment by hydrogen halides in agreement with values to be expected from electron affinities and bond dissociation energies; values were 1.88, 0.62, 0.10, and 0.03 ev for F^-, Cl^-, Br^-, and I^-. In view of the low appearance potentials for electron capture by I_2, HI, and HBr it is clear that their use in radiation chemistry for free radical scavenging is seriously complicated by the possibility of electron attachment. This possibility does not exist with the use of NO since the threshold for dissociative electron capture lies at 7 ev (33b). The possibility of simple electron attachment to form NO^- cannot be eliminated, however, since Rudolph et al. (34) found evidence for $NO + O^- \rightarrow NO^- + O$. Cloutier & Schiff (35), on the other hand, deduced a high threshold for electron attachment by NO. However one interprets these results, an ionization potential of only 9.25 ev seriously restricts the use of nitric oxide as a scavenger for free radicals in irradiated systems.

A complete study by Frost & McDowell (36) of the ionization and dissociation of oxygen by electron impact illustrates well the detail and accuracy that can be obtained by the retarding potential difference method. The four spectroscopically determined states of O_2^+ were observed, as well as an additional state at 21.34 ev. Six different dissociation processes were identified. Appearance potentials and heats of formation have been reported for the important ionic species from BCl_3, BBr_3, BI_3 [Koski et al. (37)], from SO_2 and SO_2F_2 [Reese et al. (38)], and from hydrazine and its various methyl derivatives [Dibeler et al. (39)]. A redetermination of the ionization potentials of methyl and ethyl amines by electron impact gives values appreciably higher than those from photoionization [Collin (40)]. Vilesov, Kurbatov & Terenin (41, 42) found only parent molecular ions from the photoionization of NH_3, N_2H_4, $C_6H_5CH_2NH_2$, and $C_6H_5NH_2$. Products of photodissociation found were NH_2, H from NH_3; $C_6H_5CH_2NH$, H, or $C_6H_5CH_2$, NH_2 from $C_6H_5CH_2NH_2$; none from $C_6H_5NH_2$. Collin & Lossing (43) reported ionization potentials of various branched paraffins, olefins, and di-olefins. The re-

sults parallel those from photoionization but are systematically higher. Lampe & Field (44) determined the appearance potentials and assigned processes for the important modes of decomposition of neopentane. The steps $C_3H_6^+ \rightarrow C_3H_3^+ + H_2$ and $C_2H_6^+ \rightarrow C_2H_3^+ + H_3$ were deduced from metastable ion transitions but are not consistent with measured appearance potentials. Some ions produced by electron impact contain kinetic energy. Stanton (45) considered the problem of the origin of 2 ev kinetic energy in CH_3^+ from C_3H_8 under electron impact. Coulombic repulsion from dissociation of a doubly charged fragment would require a second, high energy component, but none appears at other masses of 14 or greater. Reed & Snedden (46) found that CH^+ and C^+ from CH_3X ($X = H$, OH, CN, Cl, Br, I) have about 3 ev of excess energy, implying a common reaction step. An electronically excited state of CH^+ was suggested.

Lossing & deSousa (47) measured the ionization potentials of n-propyl and n-, i-, s- and t-butyl radicals; observed values agree satisfactorily with group-orbital calculations. These results help clarify the problem of structures of fragment ions from alkanes. Indirect evidence had consistently indicated that $C_3H_7^+$, whether from n- or i-propyl compounds, had the $CH_3CHCH_3^+$ structure. This assumed rearrangement has now been confirmed. McLafferty discussed both the general problem of rearrangements in mass spectra (48) and results obser ved with D-labeled sec-butyl acetate (49). Other examples of rearrangment ions from numerous esters have been observed (50). Meyerson et al. (51) reported further work on the rearranged tropylium ion; using variously deuterated species of benzyl chloride and benzyl alcohol they found that the seven hydrogens lose identity. At a maximum, $\Delta H_f(C_7H_7^+)$ is 210 kcal./mole. By labeling the 5-position of n-C_9H_{20} with C^{13}, Gur'ev et al. (52) concluded that, following electron impact, excitation energy is distributed among only a limited number of degrees of freedom.

Bimolecular ion-molecule reactions have been observed in great number and variety in the mass spectrometer. Still others have been postulated. Radiation chemistry of gases thus has a great advantage over free radical kinetics in one's being able to observe single reaction steps. Tunitskii & Kuprianov (53) noted that, for many ions, decomposition lifetimes may be longer than collision times in atmospheric gases with corresponding enhancement of molecular ion participation in bimolecular processes [cf. Stevenson (24)]. They also reported the following secondary ions from methane (besides CH_5^+ and $C_2H_5^+$): C_2H^+, $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_2H_6^+$. The pressure dependence was quadratic but primary ions were not identified. A technique has now been developed for observing successive reactions in the mass spectrometer. Rudolph & Melton (54) used an α-ray source in the ionization chamber of a modified mass spectrometer to identify ionic intermediates in the α-radiolysis of acetylene at 10^{-2} mm. Hg. Ions observed were $C_2H_2^+$, $C_2H_3^+$, $C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$, $C_6H_2^+$, $C_6H_3^+$, $C_6H_4^+$, and $C_6H_5^+$; their pressure dependent abundances help to establish primary-secondary-tertiary

ion relationships since primary ions are largely depleted at the higher pressures.

An important, non-specific type of gaseous ion-molecule reaction has been designated "hydride ion transfer" by Field & Lampe (55). The reaction $M^+ + RH \rightarrow MH + R^+$ has been observed in C_2H_6, C_3H_8, $n\text{-}C_4H_{10}$, $i\text{-}C_4H_{10}$, $neo\text{-}C_5H_{12}$, and $neo\text{-}C_6H_{14}$, and in their mixtures with CH_4. Such reactions are expected to be of considerable importance in the radiation chemistry of gaseous hydrocarbons. Barker, Hamill & Williams (56) reported 20 ion-molecule reactions for 1,3-butadiene, acetylene, and acetylene-methane mixtures, as well as appearance potentials for the important primary ions of butadiene. It is of interest that the relative abundances of six secondary ions resulting from the 1,3-butadiene $C_8H_{12}^+$ complex are very similar to those of the corresponding ions (same m/e) in the mass spectrum of ethenyl-cyclohexene. Tal'rose & Frankevich (57) consider, as do others, that to be observable an ion-molecule reaction must have no activation energy. They also assume, however, that if in a particular instance of a known type-reaction $M + RH^+ \rightarrow MH^+ + R$ no secondary ion appears, then the reaction must be endothermic. Thus, by simple thermochemistry for various RH^+ and constant MH^+, $\Delta H_f(MH^+)$ or the proton affinity of M could be assigned upper and lower limits. An examination of more than 70 possible ion-molecule reactions by Tal'rose & Frankevich showed that all type-reactions $M + RH^+ \rightarrow MH^+ + R$ and $M^+ + RH \rightarrow MH^+ + R$, which are known to be exothermic, do in fact occur while reactions known to be endothermic do not occur. They also found that translational energy up to 15 ev in $C_2H_4^+$ did not lead to measurable reaction $C_2H_4^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2H_3$ for which $\Delta H = 8$ kcal./mole. Deflecting and retarding fields were used to show that there is little excess translational kinetic energy associated with the products of exothermic reactions. On this basis they find proton affinities of 180 and 193 kcal./mole for CH_3OH and C_2H_5OH respectively (58). Lampe & Field (59) maintain, on the contrary, that thermoneutrality or exothermicity is a necessary but not a sufficient condition. Using both $CD_4 - H_2$ and $CH_4 - D_2$, neither CD_4H^+ nor CH_4D^+ could be detected although they are allowed energetically.

Field & Lampe (60) measured cross sections for several reactions in mixtures of $CH_4 - HCl$ and $CH_4 - H_2S$. Minimum values of the proton affinities of HCl and H_2S are 120 and 175 kcal./mole respectively. Pottie, Barker & Hamill (61) measured the appearance potentials of the major primary ions of methyl and ethyl iodides, as well as of 12 secondary ions. Examples of relatively long-lived ($\sim 10^{-5}$ sec.) collision complexes of the type $RX^+ + RX \rightarrow (RX)_2^+$ were reported by Pottie & Hamill (62) for C_2H_5I, C_2H_5Br, C_3H_7I. Experimental evidence for a limiting, critical energy of the complex was adduced from the observed inverse dependence of $(RX)_2^+$ upon electric field strength in the ionizing region. A similar dependence was reported by Saporoschenko (63) for $N_2^+ + N_2 \rightarrow N_4^+$ in the ion source of a mass spectrometer operated at 0.1 to 0.6 mm. Hg. Since the cross section is $ca.$

10^{-9} that typically found for ion-molecule interaction, radiative stabilization of the collision complex appears likely. Using a specially designed mass spectrometer, Melton & Ropp (64) have distinguished between $A^{\pm} + B$ and $A + B^{\pm}$ reactions. A negative ion from formic acid reacts with nitrogen producing a secondary ion of $m/e = 26$, unchanged with DCOOH. Either $HC^{13}OOH$ or N^{13} gives $m/e = 27$; labeling both gives $m/e = 28$. They consider this to be the first case of a negative ion-molecule reaction observed in a mass spectrometer. Probe measurements in the afterglow of an iodine discharge lead to the surprising conclusion that the cross section for $I^- + I_2 \rightarrow I_2^- + I$ is $4 \cdot 10^{-17}$ cm.^{2} [Young (65)].

Very little work has been done on negative ion-molecule reactions. Hurst & Bortner (66) used both electron beam ($>2ev$) and electron swarm($<2ev$) experiments to study negative ions of oxygen. The possibility of direct attachment followed by collision stabilization to give O_2^- appears to be plausible. If correct, this process would be of considerable significance in oxygenated systems. Melton, Ropp & Rudoph (67) reported Cl_2^- and Br_2^- as well as Cl_3^+ and Br_3^+ from the free halogens. Henglein & Muccini (68) reported several negative ion-molecule reactions of relatively large cross section. Most of them involved O^- from SO_2. Both NO_2^- and SO_2^- were produced by electron transfer, although not by electron attachment, while $C_6H_5NO_2^-$ forms directly. Observed inequality relations between electron affinities were: $SO_2 > SO$, $SO_2 > C_6H_5NO_2$, and $NO_2 > O$.

Bennett & Dalby (69) measured the radiative lifetime of N_2^+ for the 3914 A transition. Their method involves producing excited states by electron bombardment until equilibrium with radiative decay is reached. The electron beam is then turned off and photon yield vs. time measured. This elegant technique can also be applied to free radicals.

Reactions in gases.—Magee & Funabashi (70) have developed a general theory that explicitly describes the energy of an ion as a function of the number of clustering molecules at equilibrium in the irradiated gas. Both large clusters (condensation) and small were considered and compared with experiment. In irradiated systems of chemical interest, charge neutralization will be most sensitive to clustering; minor components may cluster preferentially; ion dissociation, rearrangement, and bimolecular reactions may be effected. Schaeffer & Thompson (71) have continued their investigation of radiation-induced exchange in $H_2 - D_2$—rare gas mixtures. He, Ne, and Ar act as chain initiators and Kr, Xe as chain terminators by charge transfer. The chain propagating step is $H_3^+ + D_2 \rightarrow HD_2^+ + H_2$. Williams (72) studied the effects of low energy photoelectrons (Ag cathode) on C_2H_6, CH_4 and CH_4-Ar as dependent upon (electric field)/(pressure) ratios up to 40 v./mm. Hg. The results suggest that non-ionizing excitation by electron impact (including energy transfer from Ar) is an important primary process.

A successful correlation between the radiation chemistry of n-hexane vapor and its mass spectral fragmentation pattern has been found by Futrell (73). He postulated that each ionic fragment R^+ undergoes an ion-molecule reaction of the type

$$R^+ + C_6H_{14} \rightarrow RH + C_6H_{13}^+$$
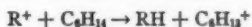
whenever it is energetically allowed. He also postulated

$$C_6H_{13}^+ + e^- \rightarrow C_6H_{13} + H$$

$$H + C_6H_{14} \rightarrow C_6H_{13} + H_2$$

followed by dimerization and disproportionation for all alkyl radicals. The yields of ten products are accounted for, as well as the effects of ethylene and oxygen in diminishing yields of H_2, C_4H_{10}, C_5H_{12}. The major gaseous products of ethylene radiolysis were found by Lampe (74) to be C_2H_2, H_2, n-C_4H_{10}, and C_2H_6. These products, however, represent only one-third of the ethylene consumed. Yields are independent of pressure; addition of argon does not change the composition of product, although absorbing and transferring energy. In mixtures of $Ar-H_2-C_2H_4$, specific H-atom initiation occurs, presumably through ArH^+ formation. The known ion-molecule reaction $C_2H_2^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2H_2$ may account for acetylene. Mikhailov et al. (75) found mainly C_4H_{10} and C_2H_2 from electron bombardment of C_2H_4, but CH_4 and H_2 from α-radiation. No hydrogenation occurs with a mixture of $3C_2H_4/1H_2$. Yang & Manno (76) obtained results that support Lampe's proposed mechanism since 5 per cent of nitric oxide in ethylene completely suppressed formation of C_2H_6 but did not affect the yield of C_2H_2. Since yields of H_2 and n-C_4H_{10} were also unaffected, the possibility of corresponding ion-molecule reactions must be considered.

These authors have also used nitric oxide to explore the role of free radical processes in the radiolysis of methane, ethane, and propane (77). For propane the fractional free radical contributions to the formation of various products were: H_2, 0.58; CH_4, 0.36; C_2H_6, 0.32; i-C_4H_{10}, 0.91; i-C_5H_{10}, 1.00. There is inconclusive evidence supporting the reaction $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$. Dorfman & Wahl (78) investigated the radiolysis of acetylene to determine whether different primary processes could account for the products cuprene and benzene. In mixtures of acetylene with helium ($He > > C_2H_2$), where energy transfer could ionize but not excite acetylene, not more than 0.1 per cent of C_2H_2 reacting produced C_6H_6. This implies an ionic precursor for cuprene. In the direct radiolysis the relative yield of C_6H_6 decreases at low pressures due to a wall effect. Precursors of C_6H_6 have a lifetime $\gtrless 10^{-4}$ sec.; the triplet state of C_2H_2 is probably involved.

Lucchesi & Heath (79) studied the γ-induced gas-phase alkylation of propylene with isobutane at 55 atm. and $350-400°$. A complex mixture of products was obtained, with reaction chain lengths of 20 to 100 under conditions where the thermal reaction was negligible. The results are not inconsistent with conventional free radical kinetics. A new, radiation-induced, chain alkylation of acetylene with propane has been discovered by Bartok & Lucchesi (80). The reaction mixture was exposed to mixed pile radiation at 48×10^6 and 17×10^6 rad./hr. at 10 to 15 atm. and $250-400°$. The product was predominantly 3-methyl-1-butene; G(product) was 36 to 59. Since the corresponding thermal reaction is unknown it is difficult to distinguish between ionic and free radical chain mechanisms. Gas phase

radiolysis of C_2-C_6 alkanes by Back & Miller (81) gave similar results for x- and α-irradiation at low dose. Yields of H_2 and unsaturates are greater than had been supposed. Liquid and polymer products were practically nil. For pentane, G(pentyl) = 14.6 which can be accounted for by H-abstraction from pentane by H· and CH_3·. Ion-molecule reactions of the type $RH^+ + RH \rightarrow RH_2^+ + R$ followed by $RH_2^+ + e^- \rightarrow R + H_2$ are also considered likely.

Hickham & Berg (82) correlated the area under mass spectrometric ion current-electron voltage curves for electron attachment by halogen-containing molecules with the electric strength of the gases. Products of the electrodeless discharge of hydrazine were introduced directly into the orifice of a mass spectrometer. Compounds observed were H, H_2, N, NH_2, NH_3, N_3, N_2H_2, N_2H_3, N_2H_4 and N_3H_3. The condensate at 77°K. yielded N_4H_4 [Foner & Hudson (83)]. Harteck & Dondes (84) have considered the possibility of employing reactor radiation for the radiation chemistry of gases. In particular, the decomposition of carbon dioxide and the fixation of nitrogen from air are described. For steady-state compositions of pile-irradiated 1:1 nitrogen-oxygen mixtures at 85° the percentage composition was 25 N_2, 6.4 O_2, 43.7 NO_2, 0.48 N_2O. There is no indication of ionic reactions that form or decompose fixed nitrogen (85). Dmitriev has used both the electric discharge and electron bombardment in mixtures of nitrogen and oxygen. The primary act is considered to be ionization and dissociation of N_2. No effect attributable to ionization of O_2 was found (86). The effect of removing ions from the reaction zone confirms this interpretation (87). Electron bombardment of nitrogen-oxygen-water mixtures produces HNO_3 and N_2O, with maximum yields at 15 per cent oxygen (88). Synthesis of NH_3 in γ-irradiated mixtures of nitrogen and hydrogen also appears to depend upon energy absorbed by N_2 [Cheek & Linnenbom (89)]. Armstrong & Spinks (90) found ion pair yields approximating 10^5 for C_2H_5Br by γ-ray induced addition of HBr to C_2H_4. Initiation is considered by way of $HBr^+ + HBr \rightarrow H_2Br^+ + Br$ and various possible products from reaction between H_2Br^+ and $Br-$. Johnson & Miller (91) found G(HCl) = 3.38 for radiolysis of n-propyl chloride and 3.82 for i-propyl chloride. With added HCl[35], $G_{(exchange)}$ was 3.32 and 1.27 respectively. Kupperman & Burton (92) found energy utilization of $ca.$ 50 per cent for decomposition of n-butane in the glow discharge, with H_2, C_2H_2, C_2H_4 as major products. Temperature of the discharge was probably <100°. Results are consistent with excitation by electrons in the discharge of the low-lying electronic states of C_4H_9. The products of electrical discharge have been examined for oxygen [Herron & Schiff (93)], hydrazoic acid [Franklin et al. (94)], diborane [Kotlensky & Schaeffer (95)], hydrogen cyanide [Takahashi (96)], and methane [Eremin et al. (97)]. The spectra emitted from the solid products of electric discharges containing nitrogen at very low temperatures have been described in detail by Peyron & Broida (98). Schüler & Stockburger (99) continued the series of studies of "V spectra" of organic molecules in the elec-

tric glow discharge. Light emission appears to depend upon collision between excited and unexcited molecules.

WATER AND AQUEOUS SOLUTIONS

Irradiation of water can be described in terms of H_2, H_2O_2 (the "molecular yield"), and of H, OH (the "radical yield"). The molecular yield is relatively insensitive to concentration of scavenger and is generally ascribed to diffusion-controlled combination of radicals. With increasing solute concentration, radical combination within the track diminishes, thereby providing an effect that has been utilized both theoretically and experimentally to explore track effects. For energetic γ-rays and electrons, primary events occur in widely separated spurs (~ 10 A radius). At high linear energy transfer (LET) the spurs overlap, the track becomes columnar, the molecular yield increases at the expense of the radical yield, and solute effects diminish.

The radiation chemistry of water has been reviewed, by Dainton (100), Hart (101), and Kupperman (102). Oxygen effects in aqueous solutions, particularly the formation of hydroperoxides, were reviewed by Scholes & Weiss (103). In the radiolysis of aqueous solutions containing H_2, H_2O_2, and O_2, the "H' atom" formed by free-radical oxidation of H_2 is shown to react with O_2 much faster than with H_2O_2. The "H atom" formed by radiolysis of water reacts with O_2 and H_2O_2 at comparable rates. Barr & Allen (104) concluded that the two kinds of "H atom" may be the basic and acidic forms of H, i.e., the solvated electron and H_2^+. A comprehensive treatment of the secondary reactions of water under high energy radiation, which includes the H' proposal of Barr & Allen, has been proposed by Allen & Schwarz (105). They employ the best available primary yields together with ratios of rate constants for

$$OH + H_2 \rightarrow H' + H_2O$$
$$OH + H_2O_2 \rightarrow HO_2 + H_2O$$

and for

$$H + H_2O_2 \rightarrow OH + H_2O$$
$$H + O_2 \rightarrow HO_2.$$
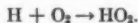
Both transient and steady-state phenomena are qualitatively and quantitatively described in a self-consistent manner in several aqueous systems and for radiation of different quality.

One view of the fate of the ejected electron has been proposed by Platzman (106, 107). According to this view electrons very quickly fall below the energy of the lowest excited state of the medium. Subsequent slowing down to thermal energy by interaction with vibrational and rotational degrees of freedom of solvent dipoles requires $\sim 10^{-11}$ sec. and includes the possibility of selective reaction with minor constituents of the system. In water it leads to a diffuse distribution of H following electron capture by H_2O. According to an alternate view by Samuel & Magee (108) electrons

quickly reach thermal energy and are recaptured by parent ions. This re-
quires initial H-OH separation to be rather less than H-H and OH-OH
separation, but for simplicity they assumed random distribution. The
theory of Ganguly & Magee (109) develops this view by describing the de-
pendence of radical and molecular yields upon LET and solute concentra-
tion. A single radical species R is assumed with $G(R) = 6$. Only two reactions
are allowed yielding R_2 or RS, where S is solute. A direct experimental test
to decide between the views of Platzman and of Magee has not been made.
Indirect tests have been made by examining track effects and are reviewed.

Flanders & Fricke (110) have employed a computer to solve the equa-
tion $\partial n/\partial t = \nabla^2 n - k_1 n^2 - k_2 n$, which had previously been proposed by Fricke
(111) to represent, by a one-radical model, the reaction kinetics associated
with track effects in the radiation chemistry of a single solute solution. The
fractional number of radicals combining with solute molecules is computed
in terms of two dimensionless parameters. Dyne & Kennedy (112) have
undertaken a detailed study of the Samuel-Magee model for the radiation
chemistry of water, avoiding the limitations of an analytical solution re-
stricted to a one-radical model by using numerical calculations. Choosing a
spur radius of 10 A gives good agreement of the model with experiment.
Isotope effects, viz. $G(H_2) > G(D_2)$, $G(-H_2O) > G(-D_2O)$, are not accounted
for by simple assumptions on the relative diffusion constants for H and D
and relative rate constants for reaction between H, H and H, OH vs. D, D
and D, OD. The combined effects happen to compensate. Special assump-
tions are required to account for the facts. The isotopic fractionation ob-
served in dilute heavy water can be accounted for by preferential dissocia-
tion of H from excited HDO. Although the relative experimental yields for
H_2 and H_2O_2 vary similarly with scavenger concentration, calculation shows
less efficient suppression for H_2. Kupperman reported an elaborate calcula-
tion program in progress (102).

Schwarz, Caffrey & Scholes have used 10 Mev deuterons, and 32 Mev
and 11 Mev helium ions to measure yields of H_2 in KBr and KNO_2 solutions,
H_2O_2 in aerated KBr, and H in solutions of H_2 and O_2 as well as of C_2H_5OH
and O_2 (113). For comparison of results with the one-radical model of Gan-
guly & Magee (109) yields were adjusted to a hypothetical basis of equal
reactivity of solute with H and OH. Using results from γ-rays to evaluate
some parameters, Schwarz *et al.* found good agreement with theory for
$G(H_2)$ but not for $G(H_2O_2)$. The observed fraction of radicals combining
agrees well with theory. At the high LET of this work a fairly sensitive dis-
tinction is possible between the uniform distribution of H atoms favored by
Platzman and the localization within spurs proposed by Samuel & Magee.
The latter view, being included in the theory of Ganguly & Magee, is
strongly supported. Increased $G(H_2)$ and $G(H_2O_2)$, relative to $G(HOH)$,
found for α-rays as against γ-rays are also shown to follow from the Samuel
& Magee model.

Hart (114) interpreted results for γ-ray radiolysis of aqueous formic acid

as supporting Platzman's proposal of subexcitation electrons. The photo-lytic product of aqueous formic acid, when it is the absorbing species, is CO. In dilute solution, when water absorbs light, or for γ-ray radiolysis, CO and H_2 only appear. However, radiolysis of 0.1, 1.0, and 26.6 M formic acid gives $G(CO) = 0.25, 0.50$, and 1.25. The disproportionately high yields, at medium concentrations, of the product characteristic of excited formic acid, were attributed to subexcitation electrons. The possibility of electron capture was considered less likely. Armstrong, Collinson & Dainton (115) used acrylamide and other solutes in light and heavy water irradiated with γ-rays. They found $G(D_2) < G(H_2)$, $G(D_2O_2) < G(H_2O_2)$. The evidence is that acrylamide reacts with precursors of H_2 but not exclusively with H. Also, $G(H) < G(D)$ and $G(OH) < G(OD)$ so that a smaller fraction of primary species form molecular products in D_2O than in H_2O. Neither spur characteris-tics nor rate constants involved in the Samuel—Magee model could be ac-commodated to these facts in the opinion of Armstrong *et al.* In the Platzman model, however, an increase in relaxation time increases the distance an electron travels before solvation, with a corresponding enhancement of radical yields. Since the relaxation time is 30 per cent greater for D_2O than for H_2O, this can account for 40 per cent more hydrogen atoms combining in H_2O than in D_2O. Their argument is supported by the very small yields observed for the radiolysis of ammonia, which has a dielectric relaxation time only one-seventh that of water.

Burton & Kurien (116) have used Br^- and Cl^- in aerated $0.8N$ H_2SO_4 with 24 Mev x-rays, $Co^{60}\gamma$-rays, 50 kev x-rays, and 3.4 Mev α-rays. Since the effect of scavenger is described by $X^- + OH \rightarrow X + OH^-$, $G(H_2O_2)$ was chosen as the best measure of diffusion effects in terms of the theory of Ganguly & Magee (109). Rate constants for the scavenging reaction above were 1.6×10^{10} and 4×10^9 liter mole^{-1} sec.$^{-1}$ for Br^- and Cl^-. Results agree substantially with theory but the yield of initial decomposition varies with particle energy in an unaccountable fashion. Graphs of log $G(H_2O_2)$ vs. log M_{X^-} show that the slope $\frac{1}{2}$ found by Sworski (117) is theoretically fortuitous. As required by theory, the slope is smaller for greater LET; in this work the slopes found were 0.15 and 0.26 for 3.4 Mev α-rays and 50 kev x-rays. Senvar & Hart (118), using an external Po^{210} source, found $G(O_2) = 0.10$, $G(H_2) = 1.45$, and $G(H_2O_2) = 1.28$ for deaerated water. This agrees with $G(H_2)$ but not with $G(O_2)$ and $G(H_2O_2)$ found by Lefort & Anta (119). Solutions of I_2 and $I_2 + I^-$ were also used. Values of $G(H_2O_2)$ are in good agreement with the one-radical model of Flanders & Fricke (110) for cylindrical diffusion.

Trumbore & Hart (120) measured $G(Fe^{+3})$ for Po^{210} α-rays in $0.8N$ H_2SO_4 up to $0.4M$ O_2. For increments resulting from increasing O_2, $G(Fe^{+3})/G(H_2O_2) = 6$ over the oxygen concentration range used, from which they conclude that HO_2 radicals escape recombination as the track expands with Fe^{+2} present. The rate constant for HO_2 combination is therefore much less than that for H combination. Within the limitations of the one-radical model, the experimental results support the diffusion theory of Flanders & Fricke

(110). Using Po α-rays, Lefort & Tarrago (121) measured $G(Fe^{+3}) = 5.5 \pm 0.1$ in $0.8N$ H_2SO_4 and $\sim 10^{-3}M$ $FeSO_4$. In air-free solutions of Ce^{+4}, Tl^+ was added to inhibit the intratrack reaction $OH + H_2O_2 \rightarrow HO_2 + H_2O$. They found $G(OH) = 0.60$, $G(H_2) = 1.57$, $G(H_2O) = 3.62$. Previous measurements of $G(H_2O_2)$ in solutions of KNO_2 showed a dependence on concentration that was in disagreement with the radical diffusion mechanism. The system has now been reexamined over a wider range of NO_2^- concentration by Schwarz & Salzman (122) who find that reaction of H with product NO_3^- accounts for the differences found between this and earlier work. Reaction rate constants are required for applications of diffusion theory. From measured initial $G(HD)$ in γ-irradiated water containing D_2, Fe^{+3}, and Fe^{+2}, Riesz & Hart (123) have calculated the ratio of rate constants for $(H + Fe^{+3}):(H + D_2)$ as 120 ± 30. By assuming the latter rate-constant to be the same in solution as in the gas phase, the former is established as $k = 48 \times 10^5$ 1 moles^{-1} sec.$^{-1}$. Several other rate constants for H atom reactions were evaluated on this basis. For dilute deaerated solutions of Fe^{+3} with Sn^{+2}, the following relative rate constants were found by Boyle, Weiner & Hochanadel (124): for

$$[Fe^{+2}+H]:[Sn^{+2}+OH] = 1:7.0; \text{ for } [Fe^{+2}+OH]:[Sn^{+2}+H]:[Sn^{+4}+H]:[Sn^{+3}+H]$$

$$= 1:5000:0.16:0.081; \text{ for } [Fe^{+2}+H_2O_2]:[Sn^{+2}+H_2O_2] = 100:1$$

Hardwick has measured yields of Fe^{+3}, H_2, H, and $-H_2O$ as functions of sulfuric acid concentration in light and heavy water as well as radical and molecular yields in oxygen-saturated formic acid solutions. A model is proposed that permits measurement of the yields of H and OH combining to reform H_2O (125). The measurement of H and OH in γ-irradiated air-free solutions of Fe^{+3}, H_2SO_4, and HCO_2H has been extended by Donaldson & Miller (126) to aerated solutions by the further addition of Cu^{+2}. The increase of radical yields with increasing Cu^{+2} and HCO_2H corresponds to intervention in diffusion-controlled radical recombinations in spurs; the results appear to support the Ganguly-Magee theory. Miller (127) employed the same aqueous systems for measuring H and OH yields at high LET. Additional evidence was found for the reaction $OH + H_2O_2 \rightarrow HO_2 + H_2O$ in the track. The simplifying assumption of stationary state kinetics, useful for γ-irradiation, is no longer adequate.

The photolysis at 2537 A of aqueous hydrogen peroxide from 0.002 to $0.02M$, with allyl alcohol (0.001 to $1M$) as scavenger, gave a quantum yield of 0.54 ± 0.05 for H_2O_2 decomposition. In the absence of scavenger the quantum yield is nearly unity [Volman *et al.* (128)].

ORGANIC LIQUIDS

Reviews were published by Schenck *et al.* (129) on comparisons of ultraviolet and ionizing radiations, by Matheson (130) on the interrelations of photochemistry and radiation chemistry, by Noyes (131) on oxygen effects in photochemistry, and by Sponer (132) on intra- and intermolecular radiationless quantum transitions.

Hydrocarbons, unlike aqueous systems, are relatively insensitive to radiation quality. Schuler (133) used $G(-I_2)$ to measure radical yields in hexane, cyclohexane, and 2,2,4-trimethyl pentane. Relative to fast electrons, decreases of 10 and 30 per cent in G(radical) were found for 10 Mev deuterons and 33 Mev helium ions. The small effect is not understood. The effect of radiation quality (0.02 to 5 ev/A) on the decomposition of n-hexane and cyclohexane is negligible, although the results for γ-rays are complicated by the influence of different dose rates [Dewhurst & Schuler (134)]. DeVries & Allen (135) found the same product distribution from liquid n-pentane for 14 Mev helium ions and for 2 Mev electrons. Products heavier than pentane contained no unsaturates and their yields were consistent with formation of free radicals by random combination. The relative yields of ten products can be accounted for (with one exception) by six adjusted parameters. Since product distribution is unaffected by radiation quality, it was concluded that small radicals seldom react with pentane to yield C_5H_{11}. The fate of H atoms, although critical, is not accounted for; efficient escape from spurs, plausible for a small atoms, and complete reaction with pentane, are indicated.

Meshitsuka & Burton (136) have largely clarified a very confusing situation relating to H-atom yields in liquid hydrocarbons, especially cyclohexane. Reported yields of $G(HI)$, from runs with I_2 as scavenger for H, had been uniformly small but it is now clear that postirradiative effects are at least partly responsible. For cyclohexane, n-hexane and benzene, $G(HI)$ is 2.1, 2.5, and 0.9. The effects of solutes and of temperature on the radiation decomposition of cyclohexane, especially for liquid products, were reported by Dewhurst (137). Initial yields are $G(C_6H_{10}) = 2.5$ and G(bicyclohexyl) $= 2.0$, unaffected by 10 atm. H_2 or liquid nitrogen temperature. With added O_2, $G(C_6H_{10}) = 0.7$, G(bicyclohexyl) <0.1; whereas with 0.04 M I_2, $G(C_6H_{10}) = 0.8$, and G(bicyclohexyl) $= 0.3$. These yields, as well as the general inability to obtain a material balance and the unexplained postirradiation disappearance of HI, demonstrate the need for further work. Dewhurst irradiated several C_6-C_8 branched chain alkanes with 800 kvp. electrons. There are no evident simple regularities in the yields of H_2, CH_4, or free radicals, which were identified as their iodides (138).

Polak et al. (139) reported electron paramagnetic resonance (EPR) evidence for H atoms in γ-irradiated alkanes at 77°K. persisting for two weeks. Their estimated concentration was one per cent that of free radicals. On kinetic grounds such stability is surprising. Charlesby, Davison & Lloyd (140) proposed two models for removal of radicals by competition with scavenger, A, as functions of intensity, I.

$$k_1(I) = k_2(R\cdot)^2 + k_3(R\cdot)(A) \qquad \text{model } a$$
$$k_1(I) = k_2'(R\cdot) + k_3(R\cdot)(A) \qquad \text{model } b$$

Choosing anthracene because its inefficiency is advantageous, they found (by comparing electron and gamma irradiation) that $G(-A)$ varies with

$\sqrt{I}$ for hexane and cyclohexane, as expected for model a. In polysiloxanes, however, there is no radiation intensity effect corresponding to model b, and it must be concluded that radicals normally disappear by a first order rate process. Implications on polymer cross-linking are considered. The radiolysis of n-heptane is inhibited by rather small additions of dibenzyl and dibenzyl sulfide; this effect was attributed to energy transfer [Brodsky *et al.* (141)].

Normal butyl mercaptan was used as a free-radical scavenger in liquid benzene, n-heptane and methyl cyclohexane [Nevitt *et al.* (142)]. Gamma irradiation of butyl bromide and powdered tin gave a large yield of $(C_4H_9)_2$ $SnBr_2$ [Abramova *et al.* (143)]. Chang, Yang & Wagner (144) irradiated 1-hexene and 1-octene in the liquid phase. The principal products were low molecular weight polymers with dimer > trimer > tetramer. Dimer was mainly monoolefin. No 2- or 3-hexenes appeared among the products from 1-hexene. These results are in marked contrast to free-radical reactions of terminal olefins, which produce rearranged non-terminal olefins and dimers containing two double bonds. Unlike irradiated paraffins, there were practically no fragmentation products. The authors postulate an ion-molecule mechanism for dimerziation or higher polymerization. The oxidation of liquid cumene from 20–60° was measured at 1 to 200 r./min. A chain reaction yielding only the hydroperoxide was linear in dose to over 1 M ROOH. Bulk polystyrene and its deaerated solutions are very radiation resistant. It is efficiently degraded in aerated solutions in CCl_4 or $CHCl_3$ [Durup *et al.* (145)]. For the x-ray induced oxidation of liquid cyclohexene at 28° and 49°, oxygen consumption varies as the square root of radiation intensity, giving peroxide as the exclusive product [Brun & Montarnal (146)].

Bach (147) has reported the effects of oxygen on the radiolysis of n-heptane, isopropyl ether, and ethyl ether. Huyskens *et al.* (148) found $G(-C_6H_6) = 4.23$ for benzene vapor at 100° using 5 to 8 Mev α-rays; for the liquid at 30°, the yield of gaseous products was 0.17 per 100 ev. Chapiro (149) reviewed critically the polymerization of vinyl monomers as a method for investigating radical yields in the radiolysis of binary mixtures. Measurement of $G(R\cdot)$ requires knowledge of propagation and termination rate constants, as well as freedom from secondary effects. Solutions of styrene in aromatic hydrocarbons or carbon tetrachloride, and methyl methacrylate in methyl acetate, carbon tetrachloride, or benzene, have been examined with respect to the kinetic effects of radiation intensity [Chapiro *et al.* (150)]. Radical yields in benzene solutions of fluorocarbons are small over the entire concentration range but they are very large in benzene-carbon tetrachloride, when both are measured by DPPH (diphenylpicrylhydrazyl). In contrast, polystyrene degradation in fluorobenzene-benzene does vary with solvent composition [Feng (151)]. Baxendale and co-workers (152) have extended the use of benzoquinone and ferric chloride from methanol to other alcohols, ether, acetic acid, ethyl acetate, and cyclohexane. Decreased yields of H_2 and CH_4 were attributed to free-radical scavenging. Primary yields of H, CH_3, H_2, and CH_4 were obtained by kinetic analysis; total radical yields

were identified with G(-benzophenone) and $G(-Fe^{+3})$. Further work on the radiolysis of methanol [Lichtin (153)] has not resolved the problem of irre-producibility of product yields in the "pure" material. The effects of various solutes were also examined.

Strong & Burr (154) measured radiolysis yields of H_2, CH_4, and CO from isopropanol, acetone, and acetone-d_6 and their mixtures. The addition of acetone to isopropanol greatly diminishes $G(H_2)$ but does not affect $G(CO)$ or $G(CH_4)$. Using acetone-d_6 instead, yields of light and heavy products correspond to simple additivity. It was concluded that acetone functions as a trap for H atoms. Ausloos & Trumbore (155) studied the γ-radiolysis of CH_3COOCH_3 and CH_3COOCD_3, both liquid and vapor, as a function of temperature, dose, and added free-radical scavengers. A comparison of labeled products indicates the primary processes and hot radical effects as well as disproportionation and recombination in the track.

SOLIDS AND POLYMERS

Physical examination of irradiated rigid organic materials, especially at low temperatures, offers attractive advantages that complement chemical analysis. The principal methods used have been optical absorption spectroscopy, luminescence, conductivity, and especially paramagnetic resonance. These methods have been reviewed by Gordy (156), Livingston (157), Matheson (158), and Taylor (159). Also, a number of papers on energy transfer, which are significant for radiation chemistry, were presented at a symposium of the *Societe de Chimie Physique* in Paris, May 27–30, 1958 and have been published (160).

Rosenstock & Schulman (161) have considered theoretically the problem of radiation damage in organic solids as indicated by luminescence degradation. A model that agrees with the facts assumes a constant probability that excitation of any molecule throughout the crystal, independent of its distance from the hit molecule, will result in quenching. This requires at least 3×10^4 jumps of the excitation energy among neighboring molecules. Examination of trapped radicals by their electronic absorption spectra in irradiated rigid solutions has been used effectively to examine primary radiation processes. Chilton & Porter (162) identified radicals from γ-ir-radiated toluene and its derivatives in rigid solutions as identical with those found earlier by photolysis. The 100-ev yield of triphenylmethyl from $5 \times 10^{-3} M$ triphenylmethane was 0.17. From the concentration dependence they conclude that energy transfer to a solute molecule is 7000 times more probable than its degration by a solvent molecule. (The same results are, however, open to the interpretation that H migrates and reacts with solute 10^4 times as effectively as with solvent.) Schenck, Meder & Pape (163) have irradiated, with electrons and x-rays, plastics containing various solutes and have examined the trapped unstable intermediates spectrophotometrically at regular intervals. Polymethylmethacrylate, polystyrene, polyvinyl chloride, or like substance was dissolved with 1 to 3 per cent of aromatic amine; evaporation of the volatile solvent left clear, thin films. Inter-

mediates persist for weeks at $-80°$. The photolysis of benzophenone in plastic films and in solution is compared with radiolysis. When γ-irradiated methane at $4.2°K$. is somewhat warmed and re-examined by EPR, the four-line spectrum of CH_3 is reduced in intensity and sharpened, relative to unwarmed samples at the same concentration. One of several possible explanations is that broadening is the result of spin-spin interaction at the high, local concentrations of CH_3 which prevail in spurs [Wall et al. (164)].

Methanol and ethanol glasses which have been irradiated at $77°K$. show three-line and five-line EPR spectra. They become strongly colored and bleach readily under illumination, thereby enhancing EPR absorption. Zeldes & Livingston (165), using both normal and D-substituted alcohols, suggest CH_2^+ or CH_2OH and $C_2O_4^+$ or CH_3CHOH as possibilities. Alger, Anderson & Webb (166) have examined comprehensively EPR spectra of over 50 irradiated materials at $77°K$. comprising alcohols, ketones, ethers, esters, acids, paraffins, and alkyl halides and have measured optical absorption, luminescence, and photoconductivity. They also find that bleaching visible color centers in alcohols increases EPR absorption, but in addition, bleaching in the ultraviolet-bands markedly reduces or changes the hyperfine structure. For color centers in ethanol $G = 5$. Results of photoconductivity measurements in irradiated samples of methanol, ethanol, and acetone during bleaching were negative, although 10^{10} trapped electrons could have been detected. "Glow curves" for ketones give trap depths of 0.15 and 0.23 ev. The phosphorescence decay for acetone at $-170°$ indicates the trapped electron is approximately one mean free path distant from the luminescent species.

Polymers.—Continuing their studies on the irradiation of linear polyethylene, Williams & Dole (167) find that, above the melting point, yields of H_2, $C\!=\!C$, and crosslinking are greater than at room temperature. Postirradiation fusion of polyethylene increases vinyl decay, vinylene formation, and crosslinking. Material balance between H_2, $C\!=\!C$, and crosslinking is approached by allowing for endlinking. Dole et al. (168) reported that G (-vinyl) $= 9.6$ for linear polyethylene, concomitant with increasing G(vinyl). Vinylene unsaturation from admixed polybutadiene does not protect vinyl. They attributed the unusually large G for vinyl decay to excitation in localized regions.

Cyclization in the solid, but not molten, state is attributed to crystallinity. This effect, as well as vinylene formation, on the sole basis of temperature independence from $77–300°K$., is attributed to ionic reactions. Lawton, Balwit & Powell found for x-irradiated Marlex-50 that crosslinking occurs mainly in amorphous regions while transvinylene occurs as readily in crystalline as non-crystalline or glassy regions at low temperatures. Radicals trapped in crystals, or glass, do not readily crosslink. When warmed they become mobile, crosslink, and disappear (169). Trapped radicals, detected by infrared and EPR measurements, were found to react with O_2 or C_2H_4. Diffusion of scavenger is rapid through glassy or amorphous material. There is a large postirradiation reaction of oxygen with $G(-O_2) = 22$ that shows the necessity of removing radicals from irradiated polymers to avoid deterioration

in air (170). Worrall & Pinner (171) have chosen the irradiation of isobutene to investigate an ionic propagation reaction. Addition of various inorganic powders (ZnO, SiO₂, etc.) increases the rate without a corresponding increase in degree of polymerization. Since the site of the electron during the cationic chain propagation poses something of a problem, it is convenient to assign this function to the solid particles. Collinson, Dainton & Gillis (172) also presented evidence for γ-ray initiated polymerization of liquid isobutene at $-78°$ by an exclusively cationic mechanism. Addition of DPPH did not inhibit polymerization but benzoquinone reduced the rate to zero. The latter is assumed to promote charge neutralization by electron capture. Chain propagation in the nominally pure liquid is assumed to depend upon electron trapping at walls or dust particles. Okamura *et al.* (173) have found evidence for γ-induced ionic polymerization of styrene in methylene chloride at $-80°$. The infrared spectra of polymer obtained from electron-irradiated butadiene at 0, -40, -78, and $-180°$ are identical with each other whereas for radical propagation the *cis/trans* ratio is temperature-dependent. This difference is attributed to kinetic control of a very fast ionic process [Anderson (174)].

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QUANTUM THEORY OF ELECTRONIC
STRUCTURE OF MOLECULES[1]

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This review will cover some aspects of the recent development of the quantum theory of the electronic structure of molecules. The first two sections are devoted to the general theory for solving the Schrödinger equation for a many-electron system and its mathematical aspects; these are followed by a series of sections with descriptions of applications to atoms, small molecules, polyatomic molecules, and conjugated systems. The concluding section contains a discussion of the present status of the theory and trends for the near future.

General Theory

Basic postulates and theorems.—The stationary states of a molecular system are theoretically determined by solving the Schrödinger equation $H\Psi = E\Psi$. The classical quantum rules are replaced by natural boundary conditions, and the solution is further subjected to the Pauli exclusion principle in the form of an antisymmetry requirement. The solutions are usually of two types: in one, the normalization integral $\int |\Psi|^2 (dx)$ exists ($=1$), and in the other, the wave function is at least finite everywhere. The first type is associated with discrete energy values and corresponds to bound states, whereas the second represents the free states occurring in collision problems and is associated with eigenvalues forming a continuum. In this review we will essentially confine our interest to the bound states.

The general existence theorems for the solutions to the Schrödinger equation, with the potentials occurring in nature, have not been proven so far, but important basic work has been carried out by Kato (1, 2, 3) particularly in connection with the helium problem, which is universally used as a first test for all theories. Kinoshita (4) has pointed out the existence of formal solutions, but the actual analytic character of the wave functions is still not known, and the occurrence of logarithmic terms in many-electron functions is being discussed [Fock (5, 6); Demkov & Ermolaev (7)].

Variation principle, expansion of wave function in a complete set.—For the practical solution of the Schrödinger equation, $H\Psi = E\Psi$, the variation principle, $\delta\langle H\rangle = 0$, is used to a large extent [Hylleraas (8)]. In this equation $\langle H \rangle = \int \Psi^* H \Psi (dx)$ is the energy expectation value and also provides an upper bound for the true eigenvalue; the question of a lower bound will be discussed in a following section.

Based upon Ritz, one tries to expand the eigenfunction Ψ in molecular

theory in terms of a fixed complete basic set $\{\Phi_k\}$, so that $\Psi = \Sigma_k \Phi_k C_k$ results. If one introduces the energy matrix $H_{kl} = \int \Phi_k^* H \Phi_l(dx)$ and the overlap matrix $\Delta_{kl} = \int \Phi_k^* \Phi_l(dx)$, the variation principle leads to a system of linear equations $\Sigma_l(H_{kl} - E\Delta_{kl})C_l = 0$, having the secular equation $\det\{H_{kl} - E\Delta_{kl}\} = 0$. In this procedure, the completeness of the basic set is essential. The modern form for completeness conditions has recently been reviewed in the excellent surveys of orthogonal sets given by Tricomi (9) and Sansone (10). Today it is hardly necessary to emphasize that the set of ordinary hydrogen-like orbitals 1s, 2s, 2p, 3s, . . . is not complete unless the continuum is fully included. However, one easily obtains a convenient, complete, and discrete set by omitting the principal quantum number n in the radial variable $\rho = 2Zr/n$ [Shull & Löwdin (11)].

For truncated basic systems there are now good numerical methods available for solving the secular equations and the associated linear equations by means of modern electronic computers; the primary difficulty currently lies instead in the evaluation of the matrix elements H_{kl}. This in turn leads to the problem of molecular integrals which is reviewed below. So far, little has been done by the quantum chemists to estimate the remainder caused by the truncation of the complete infinite basis to a set of finite order, but it seems that this problem would be very essential for testing the reliability of the wave functions obtained with respect to quantities other than the energy itself.

For truncated sets, the use of non-linear parameters has been investigated by several authors including Boys, Roothaan, and Watson; it leads to improved results but requires usually rather formidable calculations by high-capacity computers. In this connection, the importance and simplicity of the correct scaling of the basis has again been stressed [Löwdin (12)]. The virial theorem $\langle T \rangle = -\frac{1}{2}\langle V \rangle$ becomes automatically fulfilled, and it is strictly proven that, in contradiction to the so-called Hellman picture of chemical binding and some results of the free-electron model, the kinetic energy of a system always *increases* when two atoms join together to form a molecule.

In the atomic and molecular applications, one often uses non-orthogonal basic sets $\{\Phi_k\}$ that are assumed to be linearly independent so that one has $\det\{\Delta_{kl}\} \neq 0$. As a measure of the linear independence of a set, one can conveniently use the smallest eigenvalue of the matrix, Δ. Investigations of some of the standard sets—r^{n-1}, $r^{n-1}e^{-r}$, e^{-nr}, e^{-nr^2} etc. for $n = 1, 2, 3,$— show that the corresponding measures quickly become exceedingly small and that the sets are actually approximately linearly dependent. This implies that the secular determinant $\det(H_{kl} - E\Delta_{kl})$ is vanishing almost identically for all values of E [Parmenter (13)]. One can remove this difficulty by various types of orthogonalization procedures [Löwdin (14)]. However, if one tries to improve the accuracy of the eigenvalues by extending the basis in an orthogonal or non-orthogonal way, it seems likely that the number of significant figures used in the calculations must be increased simultaneously.

If we cannot circumvent this difficulty, the fixed number of bits of the electronic computers available will soon put a very inconvenient limitation on the accuracy obtainable in wave functions and eigenvalues.

Perturbation theory.—If the Hamiltonian, $H = H(\alpha)$ depends on a parameter α it may be convenient to express the solution of the eigenvalue problem $H\Psi = E\Psi$ in terms of a power series, $E = E_0 + E_1\alpha + E_2\alpha^2 + \cdots$, $\Psi = \Psi_0 + \Psi_1\alpha + \Psi_2\alpha^2 + \cdots$, where the coefficients are determined by general perturbation theory. The special form, $H = H_0 + \alpha V$ provides the starting point for the conventional theory. The special properties of the Schrödinger expansion and its transforms, the Schrödinger-Brillouin formula, and their connection, have recently been studied in great detail [Epstein (15); Dalgarno *et al.* (16, 17, 18); Speisman (19); Young *et al.* (20, 21); Feenberg (22); Gray (23, 24); Schwartz (25, 26)].

For a truncated basis, the eigenvalues to the secular equation, det $(H_{kl} - E\Delta_{kl}) = 0$, may be expanded in infinite power series in α, which leads to a connection between the variation procedure and perturbation theory. The partitioning technique for solving secular equations gives a very simple derivation of the Schrödinger-Brillouin formula [Löwdin (27); Shull & Simpson (28)]. Even the coefficients in the Schrödinger expansion have been expressed in terms of an arbitrary complete basis, and this is of practical importance in cases when the eigenfunctions to H_0 are either not explicitly known or contain an inconvenient continuum [Löwdin (29)]. The coefficient E_1 is given by the relation $\partial E/\partial\alpha = \langle \partial H/\partial\alpha \rangle$. This is a generalization of the Hellman-Feynman theorem, and even the higher derivatives are given by similar simple expressions.

It should be remembered, however, that the variation method and perturbation theory actually approach the exact eigenvalues and eigenfunctions in entirely different ways that may be compared by looking at the power series expansions in α. The variation method uses a truncated basis, and the results are expressed in infinite power series in α that have approximate coefficients. The perturbation theory is, instead, truncating the power series expansion, and the exact values of a finite number of coefficients are calculated by means of a basis that is infinite and complete. The limiting procedures are therefore different in character, and this may influence the calculation of other quantities than the energy.

Upper and lower bounds for true expectation values; reliability of wave functions.—The remarks above are connected with the general problem of whether the wave functions obtained by the standard methods are reliable for describing stationary states of molecules. Since the Schrödinger equation usually cannot be solved in closed form, one has to be satisfied if the solution can be reached by a limiting procedure:

$$\lim_{n \to \infty} \Psi_n = \Psi, \qquad \lim_{n \to \infty} E_n = E.$$

The first relation depends to a certain extent on the second. Choosing the phases so that all overlap integrals $S_n = \int \Psi^* \Psi_n(dx)$ become real and positive,

one has $\int |\Psi_n - \Psi|^2 (dx) = 2(1 - S_n)$. For the ground state, this error integral is then maximized by Eckart's criterion (30):

$$1 - S_n^2 \le \{ \langle H \rangle_n - E \} / \{ E_I - E \},$$

where E_I is the energy of the first excited state. This fundamental inequality has recently also been generalized to the excited states [Shull & Löwdin (31)]. There are interesting relations among the accuracy of the wave functions, the orthogonality property, and the energy values [Trefftz (32)].

Even if the total quadratic error $\int |\Psi_n - \Psi|^2 (dx)$ tends towards zero when the energy approaches its correct value, the convergency of the sequence of wave functions Ψ_n themselves may show many peculiarities, particularly with respect to local properties.

A very sensitive test for the accuracy of Ψ_n is provided by the "local energy" $E_{loc,\,n} = H\Psi_n / \Psi_n$, introduced by Bartlett (33). This quantity has formally the same expectation value with respect to Ψ_n as the Hamiltonian itself, but reduces to a constant $(= E)$ for the exact solution Ψ. For approximate variational solutions, it varies usually between $-\infty$ and $+\infty$, and a test on H_2^+ has now been carried out [Frost, Kellogg & Curtis; (259)]. Even the form of E_{loc} in interparticle coordinates has been investigated [Frost, preprint].

It is natural that energy calculations have dominated the studies of atomic and molecular theory to date since the stationary states are described by the solutions to the eigenvalue problem $H\Psi = E\Psi$. A basic difficulty, therefore, is to find some criteria for testing the reliability of an approximate wave function Ψ_n with respect to the calculation of an arbitrary physical quantity F. This would enable us to see whether the sequence of approximate expectation values $\langle F \rangle_1, \langle F \rangle_2, \langle F \rangle_3, \cdots \langle F \rangle_n$ converges towards the true expectation value, $\langle F \rangle = \int \Psi^* F \Psi (dx)$, and to study whether upper and lower bounds for this quantity can be constructed. As we will see later, the width ΔF as defined by:

$$(\Delta F)^2 = \int | F\Psi - \langle F \rangle \Psi |^2 (dx) = \langle F, F \rangle - \langle F \rangle^2,$$

plays an important role in this connection.

Let us start with an example where a "local peculiarity" in the approximate wave functions will destroy the results. Let us consider the electric moment, $F = ex$, of a single particle, and construct the sequence of wave functions $\Psi_1, \Psi_2, \Psi_3, \cdots \Psi_n \cdots$ so that each contains a small "bump"—let us say of the form of a hydrogen 1s orbital—the magnitude of which goes to zero when n goes to infinity, so that Ψ_n and E_n approach their correct limits. By simultaneously moving the center of this "bump" further and further away from the origin, one can obtain a situation where the electric moment of the "bump" remains constant, increases, decreases, or fluctuates with increasing n. In this case, the sequence of the quantities $\langle F \rangle_n$ does not necessarily approach any limit whatsoever, and if the limit exists it may

be essentially different from the true value $\langle F \rangle$. The problem apparently is how to avoid such peculiarities and be able to guarantee that they do not occur.

The reliability problem can be solved, at least partly, if one can find useful upper and lower bounds for the true expectation value $\langle F \rangle$. Let us first consider the energy itself. For the ground state, a lower bound has been constructed by Temple (34) by utilizing the quantity $\sigma_n = (\Delta H)_n{}^2 = \int |H\Psi_n - \langle H \rangle_n \Psi_n|^2 (dx) = \langle H, H \rangle_n - \langle H \rangle_n{}^2$:

$$\langle H \rangle_n - \frac{\sigma_n}{E_I - \langle H \rangle_n} \leq E \leq \langle H \rangle_n,$$

and the formula is easily generalized to excited states. The calculation of the quantity $\langle H, H \rangle$ is a comparatively complicated problem, and applications have so far been carried out mainly on the ground state of the helium atom [Kinoshita (4, 35); Bazley (36)]. Once the two bounds are determined, there remains the problem of trying to estimate the true energy [Dickens *et al.* (37)].

For the exact solution, σ vanishes identically, but we note that one cannot draw any conclusions from this fact about the limiting behaviour of the sequence $\sigma_1, \sigma_2, \sigma_3, \cdots$ even if Ψ_n and E_n converge towards their correct limits. In order to show the possibilities for anomalies to occur, it is convenient to expand the approximate wave function, Ψ_n, in terms of the exact eigenfunctions to H, and the calculation of σ_n then corresponds to a quadratic moment problem in energy space. In analogy with the simple moment problem discussed above there could be a "bump" in the approximate wave function in energy space, and if, with increasing n, this contribution becomes smaller and smaller so that Ψ_n and E_n approach their correct values but the center of the "bump" simultaneously moves to eigenstates with higher and higher energy, the corresponding sequence $\sigma_1, \sigma_2, \sigma_3, \cdots \sigma_n$ may tend to any value desired or fluctuate arbitrarily. The relation,

$$\lim_{n \to \infty} \sigma_n = 0$$

is hence an auxiliary condition—independent of the variation principle— which will prevent the occurrence of such a peculiarity. The simultaneous minimization of $\langle H \rangle_n$ and σ_n leads to interesting theoretical and numerical problems [Kinoshita (4, 35); Hall & Fröman (260), private communication]. Even the use of σ alone as the basic variational quantity has been discussed [Preuss (38, 39)]. Although the σ condition improves essentially the quality of the wave function, it is still not sufficient to guarantee its reliability with respect to the calculation of an arbitrary quantity F. In other cases it is not even necessary.

Let us now try to construct upper and lower bounds for the true expectation value $\langle F \rangle$ by considering the difference:

$$\epsilon_n = \langle F \rangle_n - \langle F \rangle$$
$$= \int \Psi_n{}^* F \Psi_n (dx) - \int \Psi^* F \Psi (dx).$$

Introducing the two orthonormal functions, χ_+ and χ_-, by the relations $\chi_\pm = (\Psi_n \pm \Psi)(2 \pm 2S_n)^{-\frac{1}{2}}$ and using the hermitian property of F, one obtains the identity:

$$\epsilon_n = 2(1 - S_n^2)^{1/2} Re(\chi_- | F | \chi_+),$$

where Re stands for "real part of." According to the Eckart criterion, the first factor goes to zero as $[\langle H \rangle_n - E]^{1/2}$ and the limiting behavior of ϵ_n is then in accordance with the variation principle if the second factor remains bounded. In this connection, it is convenient to consider the quantity $(\chi_- | F | \chi_+)$ as the nondiagonal element in the second order matrix of F with respect to the two functions χ_- and χ_+, and several types of estimates of its absolute value are then provided by elementary matrix algebra. If, e.g., F is positive definite, one has:

$$| (\chi_- | F | \chi_+) |^2 \leq (\chi_- | F | \chi_-)(\chi_+ | F | \chi_+),$$

and if F is bounded downwards to that $\langle F \rangle \geq F_0$ holds for all wave functions, then $(F - F_0)$ is positive definite, and one obtains:

$$| (\chi_- | F | \chi_+) |^2 = | (\chi_- | F - F_0 | \chi_+) |^2 \leq [(\chi_- | F | \chi_-) - F_0][(\chi_+ | F | \chi_+) - F_0].$$

It should perhaps be observed that, for $F = H$, the equality signs holds and the relation for ϵ_n becomes an identity.

If F has neither a lowest nor highest eigenvalue, we then consider the expectation value $(\phi | F | \phi)$ for the restricted class of functions ϕ which may be found by linear combination of Ψ_n and Ψ, so that

$$\phi = [a\Psi_n + b\Psi] \cdot [a^2 + b^2 + 2abS_n]^{-1/2},$$

and introduce the assumption that at least all these quantities are bounded

$$| (\phi | F | \phi) | \leq M.$$

If this is the case, one has also $| (\chi_- | F | \chi_+) | \leq M$ which depends on the fact that, in a second order matrix, the non-diagonal element can absolutely never exceed the largest eigenvalue of the matrix, which corresponds to the expectation value of a certain function formed by linear combination of χ_+ and χ_-, i.e., belonging to the class ϕ. Under this rather general condition, one thus has:

$$| \epsilon_n | \leq 2M(1 - S_n^2)^{1/2}.$$

We note that the existence of the quantity $(\Psi | F | \Psi)$ is, of course, a necessary condition for the regularity of the limiting procedure, and that the bound-ness of the quantity $| (\phi | F | \phi) |$ is apparently sufficient to prevent the occur-rence of "bumps" and other local peculiarities in the approximate functions that could destroy the correct type of convergency.

Another approach is provided by Schwarz's inequality which gives: $| (\chi_- | F | \chi_+) |^2 \leq (F, F)_\chi$, where χ may be either χ_+ or χ_-. Replacing F by $(F - a)$ and optimizing a, we obtain $a = \langle F \rangle_\chi$ and the relation:

$$| (\chi_- | F | \chi_+) |^2 \leq (\Delta F)_\chi^2,$$

where one should use the lower of the values of $(\Delta F)^2_\chi$ obtained for χ_+ and χ_-, respectively. Hence we have:

$$|\epsilon_n| \leq 2(1 - S_n{}^2)^{1/2} \cdot (\Delta F)^2_{\chi},$$

a formula that is sometimes useful in estimating upper and lower bounds for the true expectation value. For $F = H$, one obtains a relation equivalent to Temple's formula. If the width ΔF remains bounded for either χ_+ or χ_-, the quantity ϵ_n will converge towards zero as $[\langle H \rangle_n - E]^{\frac{1}{2}}$, i.e., as a first-order quantity.

A similar method has been used by Buimistrov (40) in the special case when F is a function of the coordinates alone, but his results contain $\langle F, F \rangle$ instead of $(\Delta F)^2$, and some of his arguments in the unbounded case still seem to be open to discussion.

In this regard, we will also comment on a certain peculiarity of the theory connected with the fact that for many quantities F, there are several formulas for the true expectation value $\langle F \rangle = \int \Psi^* F \Psi (dx)$ and other quantities that are equivalent for the exact solution Ψ but give different results for approximate wave functions Ψ_n. For transition probabilities for instance, there are momentum, velocity, and acceleration formulas of highly different character [Shull (41)]. This implies that by averaging over at least two formulas and by using two positive or negative multipliers, λ_1 and λ_2, to fullfill the condition $\lambda_1 + \lambda_2 = 1$, one could always get any desired result for $\langle F \rangle$ by means of an approximate wave function. If special precautions are not taken, one could therefore obtain a poor value for $\langle F \rangle$ by means of a good wave function—differing only slightly from the exact one—or alternatively, a value for $\langle F \rangle$ in perfect agreement with experimental results available by means of a poor wave function. This dilemma occurs particularly in certain types of variational calculations. Perturbation theory using a complete basis has a somewhat stricter construction and, if the coefficients can be found in closed form, one may obtain expectation values $\langle F \rangle_n$ correct up to a certain order n. However, in order to get the total quantities $\langle F \rangle$ to be compared with experiments, there is still a limiting procedure, and a remainder problem to be studied in full detail. Therefore, further research on both the reliability problem and the limiting procedures involved seems highly important.

MANY-ELECTRON THEORY

Density matrices.—A convenient tool for simplifying the expectation values of a physical quantity F represented by an operator

$$F_{op} = F_{(o)} + \sum_i F_i + \frac{1}{2!} \sum_{ij}{}' F_{ij} + \frac{1}{3!} \sum_{ijk}{}' F_{ijk} + \cdots$$

is rendered by the density matrices Γ [Husimi (42); Löwdin (43); McWeeny (44)]. They are defined by the relation:

$$\Gamma(x_1' x_2' \cdots x_p' \mid x_1 x_2 \cdots x_p) = \binom{N}{p} \int \Psi^*(x_1' x_2' \cdots x_p' x_{p+1} \cdots x_N) \times$$

$$\Psi(x_1 x_2 \cdots x_p x_{p+1} \cdots x_N) dx_{p+1} \cdots dx_N$$

where x_i is the combined space-spin coordinate of electron i; and one obtains:

$$\langle F_{op} \rangle = F_{(o)} + \int F_1 \Gamma(x_1' \mid x_1) d_{x1} + \int F_{1,2} \Gamma(x_1' x_2' \mid x_1 x_2) dx_1 dx_2$$

$$+ \int F_{1,2,3} \Gamma(x_1' x_2' x_3' \mid x_1 x_2 x_3) dx_1 dx_2 dx_3 + \cdots,$$

where, in treating the integrands, it is understood that each operator $F_{1,2} \cdots$ works only on the unprimed coordinates and that one puts $x_i' = x_i$ before carrying out the integration. The density matrices are highly convenient, since they permit a discussion of expectation values without specifying the form of the wave function itself. They are hermitian matrices which are further antisymmetric with respect to permutations within each set of their indices.

In order to evaluate the energy $\langle H \rangle$, only the density matrix of second order $\Gamma(x_1' x_2' \mid x_1 x_2)$ is needed, and the question is whether it would be possible to formulate the variation principle $\delta \langle H \rangle = 0$ in terms of a variation of this matrix or any other Γ-matrix of order lower than N [Löwdin (43, 12); Mayer (45); Tredgold (46); Ayres (47); March & Young (48)]. It turns out that even if every wave function Ψ has a density matrix Γ, the reverse theorem is not true. With every normalizable, hermitian, and antisymmetric matrix Γ, there is associated a certain expectation value $\langle H \rangle_\Gamma$ but not necessarily a wave function Ψ. Conceptually, the Γ-space then goes outside the Ψ-space, which it fully contains. It is easily shown, that if a density matrix of order N is at least semi-positive definite, then $\langle H \rangle_\Gamma \geq E_0$. Attempts to generalize this theorem to density matrices of lower order are now being made in several places, including Uppsala and Argonne [Gilbert, private communication (261)].

The density matrices are also very feasible for discussing various types of approximations. It is a characteristic feature of the Hartree-Fock scheme, in which the total wave function is approximated by a single Slater determinant, that the density matrices Γ of all orders may simply be expressed as determinants of the first-order density matrix ρ (43). Direct methods for valuating ρ for atomic and molecular systems have been constructed by McWeeny (49, 50).

The density matrix formalism has further been used to derive a stricter basis for the statistical theory of many electron systems, Golden (51).

Angular momenta and spin.—The theory of angular momenta is of basic importance for the study of atomic, molecular, and nuclear structure. Group theory is used in the classical approach, to derive vector-coupling formulas and Clebsch-Gordan coefficients, and various aspects have been studied [Louck (52); Majumdar (53); Zel'tser (54)]. In molecular theory, the coupling of spin is of particular importance and closely connected with the concept of valency. If the Hamiltonian does not contain the spin explicitly, the wave functions will always be eigenfunctions to S^2 and S_z, and new methods for constructing such functions have been described [Berencz & Pauncz (55); Perel (56)]. In an approach recently given by the author (57, 58), wave functions of pure angular momenta M^2 are obtained by projection operators:

$$O_k = \prod_{\kappa \neq k} \frac{M^2 - \kappa(\kappa + 1)}{k(k + 1) - \kappa(\kappa + 1)}.$$

If a trial function is a mixture of components of various multiplicity, this operator will annihilate all terms except the one desired, which will survive the operation in an unchanged form. By using the turn-over rule and the relation $O_k{}^2 = O_k$, the evaluation of expectation values and matrix elements of such functions becomes particularly simple. Expansion theorems in terms of M_+ and M_- have been developed, and the operators have been used to study the spin degeneracy problem and particularly to analyse the nature of the valence bond functions [Löwdin (59)]. For a finite number of electrons, it is now possible to derive their energy, even if the overlap integrals are fully included. By means of the projection operators, simple derivations of the Clebsch-Gordan coefficients have also been given [Calais (60)].

Correlation problem.—During the last decade, there has been a considerable development of the Hartree-Fock scheme for molecular systems [Roothaan (61)], and the question of its accuracy has assumed basic importance. In this approximation, each electron is assumed to move in the field of the nuclei and in the "average" field of all the other electrons. The electrons are therefore assumed to move independently of each other, and one neglects the "correlation" between their movements that comes from their mutual Coulombic repulsion and actually causes the electrons to avoid each other. The correlation energy, or correlation error, is defined as the difference between the true eigenvalue of the Hamiltonian concerned and its expectation value in the Hartree-Fock approximation. For the ground state of certain two-electron systems, the correlation energy is remarkably constant: for the series of He-like ions, it varies slowly from -1.14 ev for $Z = 2$ to -1.197 ev for $Z = 6$; for the hydrogen molecule it amounts to -1.06 ev. Since 1 ev $= 23.07$ kcal./mole, this is an appreciable quantity. For the closed electron shells occurring in the neon-like ions, the correlation energy is around -11 ev [Fröman (62)].

For a more detailed discussion of the correlation problem, refer to a recent review by the author (63). Here we will only mention some special aspects connected with the asymptotic behaviour. By definition the correlation energy is more of a mathematical than a physical quantity, and it shows some peculiarities associated with the fact that the Hartree-Fock scheme itself breaks down for certain types of systems. Let us consider a diatomic molecule with the internuclear distance R. The correlation energy seems to be fairly constant around the equilibrium $R \approx R_0$, but, with increasing R, its absolute value increases rapidly, depending on the breakdown of the entire molecular orbital description—for the hydrogen molecule, e.g., it approaches the limit -7.737 ev.

It seems feasible to expand the correlation energy for atomic systems in terms of powers of $1/Z$ and, for closed shells, this expansion starts with a constant term, so that

$$E_{corr} = a_0 + \frac{a_{-1}}{Z} + \frac{a_{-2}}{Z^2} + \cdots .$$

[Löwdin (12)]. This depends on the fact that, in the expansions for the exact eigenvalue and the Hartree-Fock energy, the quadratic and linear terms in Z are identical and cancel in forming the difference. For atomic systems having valence electrons in unfilled shells, Shull & Linderberg (262) have recently shown that the expansion for E_{corr} contains also a linear term in Z. The Hartree-Fock expansion does not have the same linear term as the exact eigenvalue because for $Z = \infty$ there are several Slater determinants containing various combinations of ns, np, nd, $\cdots$ orbitals having the same total energy, which then splits for finite values of Z. This result is also of great importance for the molecular theory.

The correlation problem is studied extensively in many centers all over the world. It is closely connected with the problem of finding wave functions of higher accuracy than the Hartree-Fock scheme itself.

Expansion theorems for the total wave function.—In order to reach beyond the Hartree-Fock approximation in atomic and molecular theory, one essentially uses expansion methods related to the variation technique or to the perturbation theory that has been discussed in general above. Here we will only comment on features that are characteristic for many-electron systems. The methods using special coordinates, which have been so successfully developed for two-electron systems (He, H_2), have not been generalized so far to many-electron systems and will instead be reviewed in a following section.

In applying Ritz's method to a many-electron system, one starts by introducing a spin-orbital basis consisting of a complete system of one-electron functions (spin-orbitals). By considering only one coordinate at a time as variable, one can expand the many-coordinate function into products of such spin-orbitals—one for each coordinate. Applying the anti-symmetrization operator $A = (N!)^{-1/2} \Sigma_P (-1)^p P$ to each side of such an expansion, one can show that it is possible to expand every antisymmetric wave function Ψ into an infinite sum of Slater determinants built up from the spin-orbital basis (43). Such a technique, using "superposition of configurations," is frequently used in atomic and molecular theory. If the series is truncated after the first term and the spin-orbitals involved are optimized, one obtains the ordinary Hartree-Fock approximation.

If the state under consideration has certain symmetry properties, one can often conveniently rearrange the configurational expansion by applying the projection operator O, associated with the symmetry, to the expanded form of the wave function, which is then expressed in terms of projections of Slater determinants [Löwdin (63), Nesbet (64)]. The projection operator O, fulfilling the relation $O^2 = O$, may be either of group theoretical nature [Wigner (65)] or of the simple product type found feasible for angular momenta (57, 58). If the series is truncated after the first term and the spin-orbitals involved optimized, one obtains a generalization of the Hartree-Fock

scheme, in which the total wave function is approximated by a projection of a single Slater determinant. For atoms and molecules, one can then remove the restriction of the assumption about "doubly filled orbitals" and let the electrons have different orbitals for different spins, [Löwdin (65a)], which essentially diminishes the correlation error (57, 58). The first applications of this approach were to two-electron systems and to the benzene molecule, but recently the applications have been extended to the lithium and beryllium atoms and related systems by Matsen and his collaborators (66, 67) and by Burke & Mulligan (68).

In order to improve the convergency of the configurational expansions, an attempt has been made to introduce a correlation factor $g = g(r_{12}, r_{13}, r_{23} \cdots)$ that is a symmetric function of all the interparticle coordinates, nodeless and subject to the condition that the quotient Ψ/g should still be normalizable. This means that one can apply the expansion theorems given above to the antisymmetric function Ψ/g. The choice of g is important, since it should represent the "Coulomb holes" caused by the electronic correlation. Denoting the ordered configurations by the symbol κ and the corresponding Slater determinants by D_κ, we hence obtain four expansion theorems:

$$\Psi = \sum_\kappa C_\kappa D_\kappa, \qquad \Psi = \sum_\kappa C_\kappa (O D_\kappa),$$
$$\Psi = g \sum_\kappa C_\kappa D_\kappa, \qquad \Psi = g \sum_\kappa C_\kappa (O D_\kappa).$$

The coefficients C_κ are, of course, different in different expansions and may be determined by the variation principle. Even Wigner's classical theory for electronic correlation and Bohm and Pines's plasma model are related to these forms [Krisement (69)].

If these expansions are truncated after their first term and the spin-orbitals involved are optimized, one obtains various generalizations of the Hartree-Fock scheme. To show the relative power of the different approaches the following table gives a survey of the errors in the energy of the ground state of helium in kcal./mole:

Scheme:	$\Psi \approx D$,	$\Psi \approx OD$,	$\Psi \approx gD$,	$\Psi \approx gOD$;
Error:	26.3,	16.0,	2.3,	1.2.

Perhaps it should be remarked that, in this particular case, one has chosen $g = 1 + \alpha r_{12}$ and has only used spin projections [Löwdin & Rédei (70)]. Other applications will be reported below.

Natural spin-orbitals.—If the spin-orbital basis for the configurational expansions is not chosen in a way that is well suited to the problem, the convergency may become exceedingly slow. In this connection, it is of essential importance to try to transform the basis so that the convergency becomes as rapid as possible, and certain properties of the first-order density matrix $\Gamma(x_1'|x_1)$ seem to be essential for this purpose. One can determine this matrix by means of an arbitrary basis $\{\Psi_k(x)\}$ so that

$$\Gamma(x_1'|x_1) = \sum_{kl} \Psi_k^*(x_1') \Psi_l(x_1) \gamma_{kl},$$

where the coefficient γ_{kk} may be interpreted as the occupation number for the spin-orbital Ψ_k. If U is the unitary transformation bringing the coefficient matrix (γ_{lk}) to diagonal form (n_k), the functions $\chi_k = \Sigma_a \Psi_a U_{ak}$ are called the natural spin-orbitals [Löwdin (43)]. They diagonalize the first-order density matrix

$$\Gamma(x_1' \mid x_1) = \sum_k \chi_k{}^*(x_1')\chi_k(x_1)n_k,$$

and are further characterized by having maximum occupation numbers n_k. If the natural spin-orbitals are introduced as a basis, the total wave function Ψ becomes expanded in its "natural" form, which is characterized in at least one sense by a property of optimum convergency (63).

For two-electron systems, the natural spin-orbitals are of particular importance since they also diagonalize the wave function Ψ itself, which becomes a quadratic form of principal type having term-by-term optimum convergency [Löwdin & Shull (71)]. Applications have so far been carried out to the helium problem [Shull & Löwdin (72)], to the hydrogen molecule [Shull (73), Eliason & Hirschfelder (74)], and to the van der Waals forces [Hirschfelder & Löwdin (75)].

General self-consistent-field theories; Brueckner approximation.—The theory developed by Brueckner and his collaborators in connection with their studies of the nuclear shell structure shows that there are natural generalizations of the Hartree-Fock scheme along other lines, which are based on the properties of the scattering operator t. By introducing certain self-consistency requirements, one can show that there exists a system of basic orbitals which are such that both the total energy and the corresponding wave function get a particularly simple form closely related to the one-particle-model. For an N-electron system, the scattering operator may be generally written in the form

$$t = \sum_i t_i + \frac{1}{2!}\sum_{ij}{}' t_{ij} + \frac{1}{3!}\sum_{ijk}{}' t_{ijk} + \cdots,$$

in analogy to the previously mentioned expansion of the Hamiltonian. In the standard Brueckner approximation, only the first two terms in the expansion of t are considered, but in principle there are no difficulties in also including higher terms. The problem of the connection between the self-consistent-field orbitals obtained in this way, the Hartree-Fock orbitals, and the natural orbitals seems to be of essential interest.

The application of the Brueckner scheme to atomic and molecular systems involves considerable mathematical and numerical difficulties. However, particularly the self-consistent-field theory based on the exact scattering operator may be of importance for formulating one-electron-models in molecular and solid-state theory, e.g., a formal Hückel theory for conjugated systems, or a band theory for crystals. The terminology of the Brueckner scheme has previously been very different from the one used in molecular theory, but recently work has been carried out to connect the new approach

with perturbation theory and the theory of superposition of configurations [Rodberg (76), Nesbet (77)].

Applications to Atoms

Helium.—The problem of the structure of the helium atom is of essential interest in comparing the most advanced results of quantum theory with experience. In this connection, one can study the accuracy of the unrelativistic Schrödinger equation and the importance of relativistic effects, Lamb shift, and other corrections. Since the problem has been investigated in such detail, it provides an ideal first test for most many-electron theories. Some basic results concerning the nature of the eigenfunctions and the character of the energy spectrum have already been quoted [Kato (1, 2, 3)]. The logarithmic terms introduced by Fock (5, 6) have proven to be of importance also in the variational calculation of the ground state energy [Hylleraas & Midtdal (78)].

Hylleraas's classical expansion for the ground state was a power series in the three variables $s = r_1 + r_2$, $t = -r_1 + r_2$, and $u = r_{12}$ and recently Kinoshita (4, 35) has essentially improved his result by going over to the variables s, $p = u/s$, $q = t/u$, i.e., to a series containing also negative powers of s and u. By introducing perimetric coordinates, Pekeris (79, 80) has now extended the helium calculations still further by several orders of magnitude; his last wave function consists actually of 1078 terms. The solution of a secular equation of this order represents a formidable numerical problem, even if the energy matrix has been constructed so that a large number of elements are vanishing.

In connection with the helium problem, the method of superposition of configurations is mainly of theoretical interest in order to study its potentialities with respect to more complicated systems [Shull & Löwdin (72)]. It turns out that the standard angular expansion is comparatively slow to converge, even if non-linear parameters are used [Nesbet & Watson (81)]. High angular terms including $l = 14$ have been reached by introducing an iterative element in the expansion method [Tycko, Thomas & King (82)].

Hylleraas (269), in his classical papers, has already essentially improved the convergency of the configuration expansion by introducing simple correlation factors $g = g(r_{12})$ of the type $g = \exp(\alpha r_{12})$ or $g = 1 + \alpha r_{12}$. New results along this line have recently been obtained by several authors [Green *et al.* (83, 84); Roothaan (85), preprint; Löwdin & Rédei (70)]. A study of the correlation effects in two-electron atoms has been given by Kirzhnitz (86).

Even the excited states have been treated, and a variational calculation of the 2^3S state has been carried out [Traub & Foley (87)]. The metastable states of for instance the type $(2s)^2$ for He and/or H^- have also been studied [Holøien (88, 89, 90); Dalgarno (91); Gray & Pritchard (92)]. It should be observed that many papers on helium contain results concerning the He-like ions in general.

Various types of perturbation techniques have been tested on helium [Gray (23, 24, 93)]. Several other papers on helium have also been quoted in connection with the general theory.

Atomic Hartree-Fock calculations.—In the study of the structure of many-electron atoms, the Hartree-Fock calculations continue to play a dominating role. For a survey of earlier work, refer to some recent reviews [Hartree (94); Knox (95)]. The interpolation problem has been studied in great detail [Löwdin (96), Froese (97), Hartree (98)]. A simple transformation formula for the kinetic energy has been given [Freeman & Löwdin (99)], and a new representation of the exchange terms by means of a quasi-potential has been described [Hartree (100)].

Radial wave functions with exchange have been calculated for Ne and for Va^{2+}, Kr and Ag^+ by Worsley (101, 102). Excited states of carbon and oxygen have been studied [Nicklas & Treanor (103)], as well as the states $(2p^53s)$ for neon and $(3p^54s)$ for argon [Gold & Knox (104); Knox (105)].

Analytic Hartree-Fock functions have further been evaluated by Watson (106, 107) for the iron-series elements and for O^{2-} in a stabilizing environment. A special expansion technique was used. In addition, preprints show that good analytic functions for the elements of the first period are becoming available in several places.

Statistical model.—The Thomas-Fermi (-Dirac) method does not render such a detailed description of atomic structure as the Hartree-Fock scheme but gives many times a very useful first approximation [Golden (108); Gombás (109)]. An approximate analytic solution has been found [Tietz (110)], and the asymptotic behaviour for large atomic radii has been studied [Gilvarry & March (111)]. Kobayashi (112) has investigated the Thomas-Fermi model for positive ions, and even applications to complex ions have been carried out [Kamimura *et al.* (113)]. The problem of including correlation effects in the model has also been considered [Tomishima (114); Lewis (115)].

Atomic properties in general; wave functions of higher accuracy.—The problem of the atomic scattering factors has been studied in a series of papers by Freeman (116 to 119) who has also discussed the effect of spherical and nonspherical charge distributions. Most scattering factors are actually calculated in the Hartree-Fock approximation, and the effect of correlation on the scattering factors for He-, Li-, and Be-like ions has been investigated by Hurst *et al.* (120, 121). He has also studied the coherent atomic scattering factors for the LiH crystal field [Hurst (122)].

The polarization of the He-like ions has been treated by Dalgarno (123); Sundbom (124) has determined the electronic polarizability of lithium, calcium, and scandium.

The theory of atomic spectra is still not in a very satisfactory form since it requires highly accurate wave functions. The anomalies in the "Slater ratios" for carbon, nitrogen, and oxygen have been treated by a so-called two-electron state model [Yutsis *et al.* (125)]. The theory of the angular part of the wave functions has recently been simplified by use of the previously mentioned projection operators for constructing states of pure angular momenta [Fieschi & Löwdin (126)]. Layzer (127) has developed a screening

theory of atomic spectra, and semi-empirical formulas for the negative atomic ions have been constructed [Johnson & Rohrlich (128)]. Some excited states have been calculated by Horák (129), and simple analytical wave functions have been given for Be, Ne, Na^+, and for the He-like ions by using Slater orbitals with non-integral principal quantum numbers [Saturno & Parr (130)]. The Slater parameters for the elements of the first long period have further been discussed by Brown (131).

For a more detailed survey of the recent development of the theory of the electronic structure of atoms, we refer to another review by the author (132).

APPLICATIONS TO MOLECULES

Hydrogen molecule.—The theory of the ground state of H_2 is important both as a test case for molecular theories and as the simplest example of a covalent bond. Extensive calculations following the lines of James & Coolidge (263) have been carried out by Kolos & Roothaan (264) and were discussed at the Boulder meeting. His dissocciation energy (De) calculation is in excellent agreement with experience despite the fact that the effect of the nuclear motions had so far not been included. These corrections are appreciable but seem actually to cancel each other to a large extent [Fröman (265)].

Most wave functions for H_2 have now been interpreted in terms of natural spin orbitals [Shull (73); Eliason & Hirschfelder (74)]. Using this approach, Shull (133) has recently discussed and refined the concepts of covalent and ionic character of a bond. The correlation in H_2 has also been studied by Shull (134), and the method of correlation factor has been successfully used by Kolos (264).

Single-center wave functions for H_2 have been studied [Hagstrom & Shull (135)], but the results do not seem too encouraging. Also H_2^+ has been studied by this approach [Chen (136); Howell & Shull (137)]. An investigation of floating wave functions for H_2^+ and H_2 with corrections of previous results shows that the new energies are disappointingly high [Shull & Ebbing (138)].

Self-consistent-fields for H_2 have been studied [Berthier (139, 140)].The electric and magnetic properties of H_2 have also been investigated [Das & Bersohn (141); Weltner (142); Hameka (143)].

The negative hydrogen molecule ion H_2^- is of great interest from the point of view of the astrophysicists, and its ground state and low excited states have been studied [Fischer-Hjalmars (144), Gupta (145)].

Atoms in molecules; united-atom model.—Artmann (146) has discussed the importance of the atomic Hartree-Fock functions as a basis for investigating molecular properties. The problem of the connection between hybridization, polarization, and electronic correlation for the chemical bond has been treated by Berencz (147). Preuss (148) has further developed his method of "atomic associations" and also studied the use of Gaussians in this connection (preprint).

The one-center scheme or united-atom model has recently been extensively investigated by several authors [Chen (149); Gáspár *et al.* (150, 151); Bingel (152); Wulfman (153); Clinton (153a) (preprint)]. Applications to H_2^+ and H_2 have previously been reported (136, 137). It seems as if the approach would be valuable from qualitative points of view, but it is difficult to reach high quantitative accuracy with the results.

Diatomic molecules.—The simplest diatomic molecules are the hydrides, and several of them have recently been studied both in the Hartree-Fock approximation by using the MO-LCAO-scheme and in higher accuracy by means of superposition of configurations. The LiH molecule has drawn the attention of several authors [Karo & Olson (154); Karo (155); Basu (156); Ormand & Matsen (157); Platas & Matsen (158, 159)]. An electron-population analysis has been carried out by Karo (160), who has also investigated the excited state $^1\Sigma^+$ from this point of view (preprint). Also, the dipole moment has been determined [Hurst, Miller & Matsen (161)].

The same methods have been applied to the HF molecule by Karo & Allen (162, 163), and an electronic population analysis has been carried out (159). The BeH radical has been treated by Aburto *et al.* (164), using a method of self-consistent-field. The correlation correction in CH, NH, and OH has been studied by Krauss & Wehner (165), and the excited states of BH, CH, OH, and FH have been investigated by Hurley (166). It seems as if the basic properties of the first-row hydrides are now fairly well understood.

There has been a great deal of work on the diatomic molecules of the first-row atoms, and a survey was given by Ransil (266) at the Boulder meeting. Here should be mentioned a LCAO-MO SCF study of B_2 [Padgett & Griffing (167)], an investigation of the open-shell ground state of He_2^+ [Csavinszky (168)], two treatments of N_2 [Singh (169), Gombás (170)], and finally studies of different properties of NO [Mizushima (171), Brion *et al.* (172)]. The question of the dipole moments of diatomic molecules has also been considered [Gray & Pritchard (173); Trischka & Salwén (174)].

Molecular integrals.—The recent rapid progress in molecular calculations depends to a large extent on the fact that one has now overcome the bottleneck represented by the calculation of molecular integrals [Mulliken & Roothaan (175)]. As reported at the Boulder meeting, fully automatic programs for two-center integrals are now available in several places, and even the problem of evaluating three- and four-center integrals can be handled in a fairly satisfactory way. Important contributions have been given by the Kotani group in Tokyo, the Coulson group in Oxford, the Chicago group under Mulliken and Roothaan, the Slater group and particularly Barnett at M.I.T., the Hirschfelder group in Madison, the Matsen group in Austin, the Eyring group in Utah, and further by Boys, Rüdenberg, Sahni, Nesbet, Merryman, and several others. It should be observed that the results are made generally available either in the form of formulas, as tables, or by offering the possibility of using an automatic program. The latter type is perhaps becoming dominant and has only the drawback that it ties the solution

to a definite electronic computer or at least to a certain computer language. A full account of this problem would require its own review, and here we will only mention a few recent papers.

Kotani's work on the two-center integrals has been extended by Kimura & Tida (176), and the two-center exchange integrals have further been discussed by Tauber (177). Three- and four-center integrals have been investigated by Barker & Eyring (178); La Budde & Sahni (179); Barnett (180, 181); and Richardson (182). Miller, Gerhauser & Matsen (183) have collected some of their results in a book containing tables of molecular integrals. Some approximate methods for estimating molecular integrals have finally been studied by Huzinaga (184).

Small molecules.—Under this heading, we will consider the recent work on three- and four-atomic molecules. Different aspects of the quantum mechanics of the H_3 complex have been treated by several authors [Barker, Eyring *et al.* (185 to 187); Meador (188); Kimball & Trulio (189); Griffing *et al.* (190)]. Kaplan (191) has studied the electronic structure of the NH_3 molecule by the MO-LCAO-SCF procedure, and Hartmann & Gliemann (192) have determined the bonding properties of CH_3^-, NH_3, and OH_3^+ by a modification of the united-atom model. The magnetic properties of H_2O have been investigated [Das & Ghose (193)]. A molecular orbital study of the planar Be_4 complex indicates that it is unstable [Cloney & Dooling (194)].

Mulliken (195) has finally given a survey of the properties of the lower excited states of N_2, CO, C_2H_2, HCN, CO_2, CS_2, and O_3 based on MO-LCAO calculations. By using equivalent orbitals, Linnett (196) has also discussed the lower states of C_2H_2, HCO, and NH_2. The quantum-mechanical calculations are of essential help in getting qualitative aspects on the properties of these molecules, but the wave functions are still far from being accurate.

Polyatomic molecules; saturated hydrocarbons.—It is clear from the previous discussion that the solution of the Schrödinger equation for a polyatomic molecule must be a very difficult problem. A survey of the attempts to date was given at the Boulder meeting by Allen & Karo (267). The most interesting recent development is probably the variational treatment of HCHO carried out by Foster & Boys (197) and discussed at the same meeting. In a series of papers now available in preprint, these authors study the method of superposition of configurations for a range of CH_2 systems and present a new method for choosing basic orbitals so that they become well suited for describing the problem. Of particular importance are orbitals that are approximately invariant from one molecule to another, and it will be interesting to see their connection with the natural orbitals and the Brueckner functions.

Mention should also be made of some recent papers on molecular theory in general. Parks & Parr (198) have proposed a model for the electron pair bond, of which the valence bond and molecular orbital methods are special cases. The general use of molecular orbitals has been discussed by Huzinaga (199), and the non-orthogonality problem in the valence bond theory has

been considered by Mizuno & Izuyama (200). A general formalism for calculating one-electron properties has been given by Karplus *et al.* (201), and Kolos (202) has studied the electron density distribution in molecules. For treating polyatomic molecules, Allen (203) has proposed the use of basic orbitals consisting of both Gaussians and exponentials.

Among applications to be mentioned, Yamazaki (204) has given a valence bond calculation of protonated methane CH_5^+, and Del Re (205) has determined the charge distributions in some saturated organic compounds by the MO-LCAO scheme.

Intermolecular forces.—The problem of the van der Waals forces between hydrogen atoms in ground state and excited states has recently been re-examined [Hirschfelder & Löwdin (75); Linder & Hirschfelder (206)]. The additivity of the van der Waals forces has been discussed by Sparnaay (207). Keyes (208) has constructed a one-parameter family of Morse potentials for excited states of diatomic molecules, and the interaction between oxygen and nitrogen in the forms O–N, O–N$_2$, and O$_2$–N$_2$ has been studied by Vanderslice *et al.* (209).

Hydrogen bond.—For a detailed discussion of the development of the the theory of the hydrogen bond, we will refer to a recent survey by Coulson (210). Here only a few papers of a more theoretical nature will be mentioned [Fischer-Hjalmars & Grahn (211); Hofacker (212); McKinney & Barrow (213); Grahn (214); Bratoz (215)].

Conjugated systems.—In this important field, there have recently been several excellent survey articles. Coulson has written about the modern concept of conjugation (216) and also about steric effects (217). Longuet-Higgins gives a description of the theory of some π-electron systems (218), discusses some recent developments both in molecular-orbital theory and the interpertation of the spectra of conjugated systems (219), and explains qualitatively some properties of free radicals (220). The electron-gas theory of the color of natural and artificial dyes is surveyed by Kuhn (221). The recent book by Preuss (222) gives a general description of the methods used in molecular physics and particularly their applications to aromatic hydrocarbons.

Since the recent work on conjugated systems is further reported in this annual review under several other headings including molecular spectra, spin resonance, etc., we will here mention only a few selected papers of particular theoretical interest. Thus, Nagahara (223) has given a quantum-theoretical study of the nature of single, double, and triple bonds between carbon atoms. Simpson (224) studies the actual background for the formal Hückel theory for π-electron systems by means of perturbation theory; it would be of interest to investigate the connection between his ideas and the previously mentioned Brueckner theory. The valence bond theory of benzene has been re-examined by Hameka (225) and applied to its spectra. Formulas for secular equations and density matrices have been given by

Fukui *et al.* (226, 227). Some useful approximations are discussed by Baba (228) and Stewart (229).

The question of the electronic structure of the aromatic hydrocarbons, the charge and bond orders, and the reactivity indices are still paid a great deal of attention [Pullman & Effinger (230); Bessis *et al.* (231); Fukui *et al.* (232)]. The structures of naphthalene and anthracene have been studied in detail as typical examples by the self-consistent-field method [Kolboe & Pullman (233); and Fukui, Morokuma & Yonezawa (268)]. The theory of the spectra of these hydrocarbons and their negative ions has been investigated by several authors [Hedges & Matsen (234); Balk *et al.* (235); Hameka & Oosterhoff (236); Hoijtink (237); Zandstra (238)]. Liehr (239) studies the interaction of vibrational and electronic motions, and Bratoz & Besnainou (240) consider the perturbation of the carbonyl frequency through different environments. Payette & Sandorfy (241); investigated the electronic structure of the ketones; their spectra are also discussed (236).

Various problems concerning the conjugation problem itself have been studied. Berry (242) considers the importance of conjugation and polar effects in butadiene. The alternation of bond lengths in long conjugated compounds is an interesting phenomenon [Longuet-Higgins & Salem (243); Ooshika (244)]; the collective oscillations of the electrons in such long compounds have been treated by Mizuno & Izuyama (245) by using Tomonaga's sound wave method. The effect of deuteration on the properties of conjugated systems have been investigated by Pauncz & Halevi (246, 247). Combet-Farnoux & Berthier (248) determine the resonance energy of such systems as $(CH_5)^-$ and $(CH_7)^+$.

Hyperconjugation is given a simple molecular-orbital treatment by Streitwieser & Nair (249). A novel type of aromaticity is further considered by Craig & Paddock (250). Some steric effects are studied by Asgar & Coulson (251).

Two papers on the free-electron model, in addition to Kuhn's review (221), should be mentioned [Platt (252); Baur (253)].

Other fields connected with molecular structure.—There are several other fields of great interest connected with the quantum theory of molecules that will not be explicitly reviewed here. For lack of space, they will be mentioned only in connection with the names of the principal investigators to be used in seeking out their work with the aid of *Chemical Abstracts*. In crystal field theory there has recently been a great deal of activity by Hartmann and his group, Ballhausen, Liehr, Klixbüll-Jørgensen, Koster, Griffith, and others. Theoretical investigations on spin resonance have been carried out by Pople, Longuet-Higgins, Orgel, Karplus, Haering, Hameka, Gouterman, Lykos, and several others. Scattering theory for intermolecular collisions has been investigated by Mason & Vanderslice, Bates, Hirschfelder and his group, and others. The theory of carcinogenic activity and the problem of the electronic structure of compounds active in chemotherapy have

been further developed by Pullman & Pullman with contributions by Fukui and other authors. Biochemical aspects have further been discussed by Platt, Kasha, and others. Finally, of conceptual interest is the quanticule theory for the chemical bond developed by Fajans. The important field of molecular spectra is given its own review.

Present Status of Molecular Theory and some Aspects for the Future

In conclusion, we will now make some general remarks about the present status of molecular theory and the connection between quantum chemistry and chemistry itself. The qualitative aspects have been excellently reviewed by Platt (254) in a handbook article on the chemical bond, in which he shows the essential importance of the quantum-mechanical ideas in this connection. For small molecules, the quantitative aspects are also favorable, particularly since the bottleneck of the molecular integrals has now been overcome [Mulliken & Roothaan (175)]. However, it is clear that for a polyatomic molecule it must be extremely difficult to carry through an *ab initio* calculation of the electronic structure and the energy levels by solving the Schrödinger equation and by using only the values of e, m, h, and the atomic numbers Z of the nuclei involved. Hirschfelder (255) gives a survey of other mathematical bottlenecks in theoretical chemistry the possible solution of which is really not too encouraging.

The limitations of the pure theory have also been stressed in a recent review by Hall (256). He emphasizes that, even with a rapid technical development of the electronic computers, it may be very hard to reach beyond molecules containing more than about five nuclei (except hydrogen). This means that for large systems there is a great need to let experiment help theory, but in a really correct way. The difficulty here lies perhaps in the fact that the mathematical framework is a little too flexible; it has previously been pointed out that for many physical quantities formulas exist that contain multipliers which are perfectly correct for the exact wave functions but which still can be brought into agreement with any quantity desired for approximate wave functions. If for a series of molecules, the multipliers would vary regularly, such formulas could perhaps be used for interpolation or extrapolation purposes and to guide experiments, but they would still very likely be without deeper physical meaning. If it is hard to find a good reliability criterion for the strict quantum theory of molecular structure, as seen above, it is probably still more difficult to establish such criteria for semi-empirical theories.

The nearest goal of the quantum theory of molecules is perhaps to go on with the investigation of single molecules to determine their stationary states and physical properties as accurately as possible. In this connection, it is important to try to make complete interpretations of the wave functions obtained, e.g., in terms of density matrices or a conveniently chosen spin-orbital basis. In order to approach chemistry, however, it is essential to

repeat these calculations on a series of related molecules in order to try to explain all such regularities that experiments have taught us exist in nature and that could be exemplified, e.g., by Allen's (257) pure empirical theory for deriving total energies by adding bond energies for nearest and next-nearest neighbours. Such a series of repeated calculations may also lead us to a deeper understanding of the chemical concepts themselves.

There is a certain difficulty connected with the fact that chemistry and quantum chemistry often use the same terminology for different concepts. The chemical concepts are usually operationally defined, whereas the quantum mechanical concepts are based on the existence of wave functions. Words as "atom," "bond," "electronegativity," etc. may therefore mean very different things to different people. In order to discuss the connection between the concepts in chemistry and quantum chemistry, a small panel meeting was arranged in Vålådalen, Sweden in 1958 with Pauling and Mulliken as the principal discussants. A short report of the meeting has been given by Hall (258). It was agreed that a rather wide gap exists between the two types of concepts that might be slowly overcome with additional information on both sides.

There is a certain amount of controversy arising from the differences between the quantum chemist's usually rather introspective approach to his science and the experimental chemist's desire for quick and practical results, which was somewhat in evidence at the international symposium on molecular quantum mechanics held in Boulder in 1959. A report from this meeting will be published in the April issue of *Reviews of Modern Physics*, (1960). In order to resolve this controversy, it is necessary to understand not only the methods and objective of the two approaches involved and their regions of overlap, but also the nature of the existing gap between them. In this connection, the summer schools arranged in Oxford and in Uppsala to include experts in both experimental and theoretical chemistry may have importance.

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MOLECULAR ELECTRONIC SPECTROSCOPY[1]

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The activity and interest in electronic spectroscopy grows at an ever increasing rate, stimulated by the fact that the information it gives on physical and chemical phenomena is often more fundamental than that which can be obtained in any other way. From simple, well worked out systems, spectroscopic interpretation has passed on to more complex ones and its application to the liquid and solid states is leading to a deeper understanding of the processes and phenomena in condensed phases. A review of the field cannot be comprehensive because of the increase in the number of published papers and their broad scatter through the literature. While many important papers will inevitably be overlooked it is hoped that most of the outstanding advances will receive mention.

As the subject grows, the importance of reviews in bringing together the work in related fields of spectroscopy is becoming greater and they perform an indispensable function in modern scientific literature. We shall therefore begin this report with a catalogue of important reviews that have appeared during the year.

REVIEWS

The spectroscopy of free radicals has been the subject of at least six reviews that reflect the rapid progress being made in this field. Those by Herzberg (1), Ramsay (2), and Dressler & Ramsay (3) are mainly concerned with the detailed spectroscopic analysis of the simpler radicals. Norrish (4) and Porter (5) include larger radicals in their reviews and deal with kinetic and photochemical aspects. Porter relates the absorption work to the emission results of Schüler, to electron spin resonance studies, and to other phenomena. Broida & Franklin (6, 7) review recent work on free radicals trapped at low temperatures in inert solids and include studies of their emission spectra. The reactions of electronically excited molecules in solution have been reviewed by Simmons (8), who deals with the formation and decay of electronically excited molecules and with the quenching processes that lead to chemical reactions in solution.

Recent advances in the spectroscopy of the vacuum ultraviolet have been described by Price (9). Particular interest attaches to the use of this region for direct photoionization and photodissociation studies, especially in conjunction with mass spectrometers. Extensive review articles by Stöckmann (10), Wolf (11), and McClure (12) deal with the electronic states of molecules and ions in crystals. The experimental techniques are described and the types of polarization and splitting arising from the crystal symmetry

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are compared with theoretical predictions. McClure (13), in a second article, reviews the spectra of ions in crystals and gives a comprehensive account of crystal field spectra and the charge transfer spectra of complex ions. A general review in *Discussions of the Faraday Society* (13a) is also concerned with this topic. Vodar outlines recent work on the effect of pressure on molecular spectra with particular reference to the study of intermolecular forces in gaseous mixtures (14). Articles concerned with electronic excitation in biological systems are contained in the biophysical study issues of the *Reviews of Modern Physics* (14a). Of special interest are those by Calvin (15) and Kasha (16)—see also McRae & Kasha (16a). Finally, it should be said that last year's review in this series by Platt (17) on the electronic spectra of organic molecules was one of the most comprehensive written on this topic.

DIATOMIC MOLECULES

Dieke (18) has obtained the spectra of all six known isotopic species of molecular hydrogen (H_2, HD, D_2, HT, DT, T_2) under high dispersion and varying excitation. This has led to a complete wavelength table of their spectra containing about 100,000 lines. The principal band systems were found in all six spectra and a comparison of the isotopes has resulted in the clarification of many previously doubtful points. A complete table of all the known levels is given. The Lyman bands of hydrogen have been investigated under high resolution by Herzberg & Howe (19). Precise B_v and ΔG values have been obtained for all the vibrational constants of the upper state $B^1\Sigma_u^+$ have also been redetermined.

Wilkinson (20) reports finding the "forbidden" Vegard-Kaplan ($A^3\Sigma_u^+ - X^1\Sigma_g^+$) bands of nitrogen in absorption in a path of 9 to 13 meter atm. These bands at 1689 A (7–0) and 1726 A (6–0) are incompletely resolved but show intensity alternation and distribution in agreement with theory. The positions of the band origin and each rotational line agree closely with the values calculated from the known molecular constants. This fixes the position of the triplet system relative to the ground state. Bills, Carleton & Oldenberg (21) have measured the lifetime of this lowest triplet state by a new technique. High resolution studies of four other forbidden bands of nitrogen between 1444 and 1331 A have been made by Wilkinson & Mulliken (22) and their appearance explained by perturbations with nearby states. Ogawa & Tanaka (23) report six new emission bands of nitrogen in the region 1600 to 2050 A and discuss their origin. Studies of the afterglow of nitrogen at atmospheric pressure are reported by Schulze (24). Spectra emitted from solid nitrogen condensed at very low temperatures from a gas discharge are described by Peyron & Broida (25).

In an experimental determination of the oscillator strength of the first negative bands of N_2^+, Bennett & Dalby (27) find the radiative lifetime of the upper state of the 3914 A transition to be $6.58 \pm 0.35 \times 10^{-8}$ sec. The apparent radiative lifetime of the upper state of the 3771 A transition of the second positive system of N_2 was found to depend upon the conditions of

excitation. Extrapolation to the excitation threshold yielded a lifetime of $4.45 \pm 0.6 \times 10^{-8}$ sec. Liu (26), using[16] N_2 (95 per cent), has been able to confirm the vibrational numbering of the $A\,{}^2\Pi - X\,{}^2\Sigma$ bands of N_2^+ made originally by Dalby & Douglas (27a). A potential curve has been calculated for this molecule by Grandmontagne & Eido (28). A new emission band in molecular nitrogen has been observed at 1590 A by Carroll (29). Although the B and D constants of both levels have been determined, these do not coincide with any of the known states of N_2^+, which is the most probable emitter.

Rocket-borne vacuum spectrograms have been obtained showing the absorption of the Schumann-Runge bands of oxygen from which estimates of the amount of O_2 in the upper atmosphere above 90 km. can be derived (30). No NO could be detected. A fine structure analysis of the δ and β bands of the homogeneous perturbation $C\,{}^2\Pi - B\,{}^2\Pi$ of NO has been given by Lagerquist & Miescher (31). Blue afterglows in NO that show a change in the intensity distribution of the bands on the addition of helium are reported by Barth, Schade & Kaplan (32). The chemiluminescence of the nitric oxide-ozone system is described by Greases & Garvin (33) and the electronic structure of NO is considered by Brion (34). Oscillator strengths for the nitric oxide bands in the region 1700 to 2300 A and for the Schumann-Runge bands of oxygen have been measured by Bethke (35).

The absorption spectra in the vacuum ultraviolet of fluorine and HF have been obtained by Iczkowski & Margrave (36, 37). A Rydberg series establishes the ionization potential of F_2 as 15.7ev and the dissociation of F_2 is also obtained via an extrapolation of a vibrational progression. The low value of 37.5 ± 2 kcal./mole is consistent with the ionization potential and indicates appreciable antibonding of the $(\pi - \pi)$ electrons. A spectrophotometric determination of the electron affinity of fluorine is reported by Jortner, Stein & Tremin (38) and that of oxygen by Tozer (39). The dissociation of F_2 and the electron affinity of F have also been given by Stamper & Barrow (40) as 37.72 ± 0.13 kcal./mole and 83.4 ± 2.55 kcal./gm. atom respectively.

The vacuum ultraviolet absorption spectrum of chlorine has been reported by Lee & Walsh (41). Continuous absorption in the region 2100 to 1700 A is associated with the intravalency shell transitions. Banded absorption between 1870 to 1070 A is ascribed to Rydberg transitions leading to the ground state of the molecular ion. The emission spectra of chlorine, bromine, and iodine in the region 2400 to 1400 A has been studied by Haranath & Rao (42). All the systems analysed go to the ground state. Term schemes are given. The emission spectrum of Cl_2 excited in the region 2390 to 2600 A in the presence of argon has also been reported (43). The visible emission bands of chlorine have been studied under high resolution by Rao & Rao (44). The analysis indicates that the bands belong to Cl_2^+, the lower level being the ground state. Detailed analysis of the absorption spectrum of ICl is given by Hulthén, Johanssen & Pilsäter (45).

Hurley (46) has extended his calculations on the ground states of the

first row hydrides (BH, CH, NH, OH, and FH) to include the stable excited states. The excited states are predicted with an accuracy of 0.2 ev and oscillator strengths of allowed transitions from the ground state have also been calculated. Calculations on the electronic structure of HF have also been carried out by Ballinger (47). Johns & Barrow (48) have made successful analyses of the ultraviolet spectra of HF and DF, excited in mixtures with helium, which are shown to arise from $V^1\Sigma^+ - X^1\Sigma^+$. This gives information about the rotational and vibrational levels over the greater part of the range of the ground state and yields a dissociation energy of HF of 5.86 ± 0.01 ev. Similar systems have been obtained and analysed in HCl and HBr (49). A most interesting study of the emission spectra of the diatomic fluorides of silicon, germanium, tin, and lead has been carried out by Barrow and his co-workers (50, 51). In these odd electron molecules, of which the prototype is CF (which is isoelectronic with NO), the outer electron should be antibonding and of low ionization potential. The ionization potentials of CF, SiF, GeF, and SnF are estimated as 8.91, 7.26, 7.28, and 7.04 ev respectively. Dissociation energies of the ground and ionic states are given, the latter being considerably greater than the former. New bands of CF have been observed by Kutzyak & Tatevskii (52) who have considerably extended the observations on the $A^2\Sigma - X^2\Pi$ transition originally found by Andrews & Barrow (53). An extensive rotational analysis of 24 bands of the ultraviolet system of CS has been made by Lagerquist et al. (54) from which the dissociation energy of the ground state is determined as 175 ± 7 kcal./mole.

New bands of OH emitted by a discharge through streaming water vapour have been found by Michel (55) and their rotational structure was analysed. The spectroscopy of the NH radical has been described by Pannetier & Guenebaut (56). The spectra of magnesium oxide and hydroxide between 4000 and 3600 A has been reported by Pesic & Gaydon (57) and those of the oxides of calcium by Rosen & Weniger (58). The emission spectrum of tellurium oxide is described by Purbrick (59) and an extensive analysis of the γ system of the PO molecule has been given by Rao (60). The absorption spectrum of SO and the flash photolysis of SO_2 and SO_3 has been described by Norrish & Oldershaw (61) and that of ClO by Edgecombe, Norrish & Thrush (62).

Transition probabilities.—Changes in transition probability due to the interaction of rotation and vibration in diatomic band spectra have been investigated by Learner & Gaydon (63) particularly with reference to the changes in the calculated vibrational temperatures. Relative transition probabilities are calculated for 81 bands which belong to the red CN system by Wyller (64). Nichols, Fraser & Jarmain (65) review transition probability parameters arising from combustion processes. Formulas are given for the intensity distribution occurring in $^7\Pi - ^7\Sigma$ bands of MnH by Kovacs & Scari (66). Application of the kinetic theory of gases to the study of emission spectra character has been made by Trichet (67).

Shock tubes and flames.—Clouston & Gaydon (68) discuss the shock tube

as a source of studies of emission and absorption. Roth & Gloersen (69) have studied the luminosity of shock waves in xenon producing temperatures in the range 6–11,000°K. The visible continuum they obtain is interpreted as being transitions from a stable molecular excited state to a repulsive ground state. Using a multiple reflexion technique Spokes & Gaydon (70) have obtained the absorption spectra of many materials such as benzene and formaldehyde in flat flames.

PHOTOIONIZATION

One of the most interesting recent papers has been that of Tanaka, Jursa & LeBlanc (183) who used the rare gas continua to obtain a large number of well developed Rydberg series corresponding to the higher ionization potentials of CO_2, CS_2, COS, and N_2O. These fix the lower excited states of the molecular ion, and emission bands corresponding to transitions between these states have been found in many cases (73, 74). The vacuum ultraviolet spectra and ionization potentials of a large number of hydrocarbons have been reported by Price *et al.* (138). Ionization potentials of 89 molecules determined by photoionization methods with an average accuracy of about 0.01 ev are given by Watanabe (109). The vacuum ultraviolet spectrum, absorption coefficients, and ionization potential of NO_2 have been reported by Nakayama, Kitamura & Watanabe (139). The use of vacuum ultraviolet monochromators in conjunction with mass spectrometers has been further developed by Hurzeler, Ingraham & Morrison (140). The appearance potentials of the parent and various fragment ions can be determined with greatly increased precision using photoionization instead of electron impact methods. Similar work has been carried out by Vilesov, Kurbatov & Terenin (141) who compared the effect of using electrons and photons on some aliphatic and aromatic amines. In both cases the fragmentation consisted mainly in the breaking away of hydrogen atoms. In the case of benzylamine the fluorescence spectrum of NH_2 was found, this was, however, absent for aniline. The short wavelength limit of this combined optical and mass spectrometric technique has been extended to 430 A by Weissler *et al.* (142) who analyse their results in terms of photoionization cross sections and dissociative photoionization mechanisms. Pickett and co-workers (143 to 146) have made studies in the Schumann region on a number of cyclic and normal ethers, alcohols, acetaldehyde, and acetone.

EMISSION SPECTRA OF POLYATOMIC MOLECULES

The electronic excitation by slow electrons of polyatomic molecules in a molecular stream has been described by Leach & Horani (71). They observed the spectra of CO_2^+ and N_2O^+, the latter having been previously obtained by Brocklehurst (72) and more recently examined under high resolution by Callomon (73) who showed the transition to be $^2\Sigma$—$^2\Pi$, the ion being linear in both states. The electronic energy of 3.492 ev agrees well with the difference of the first two Rydberg series limits observed by Tanaka, Jursa &

LeBlanc (30). The spectrum is the exact analogue of the transitions in CO_2^+ and CS_2^+. A detailed rotational analysis of the emission spectrum of CS_2^+ has been made by Callomon (74).

Schüler & Lutz (75) describe further developments of the experimental layout for the emission spectroscopy of organic substances in the positive column of a discharge. Investigations on the intensities of the spectra obtained with the glow discharges of substituted benzenes indicate that the excitation arises partly by electron impact and partly by collisions with excited molecules. Schüler & Stockburger (76) have also extended these studies to larger aromatic molecules and have shown that the excitation causes a splitting off of a small molecule (H_2, HF, HCl, C_2H_2, CH_4), the remainder becoming stabilized by double bond formation, ring closure, or dimerization. They also show that the second excited state of the benzyl radical discovered by Porter & Wright (77) can be detected by absorption in the glow discharge and its lifetime can be measured (78). Differences between radicals formed in the glow discharge and by photolysis in the solid state are discussed by Porter & Strachan (79). Detailed analyses have been made of the vibrational structure of the emission spectra of toluene and monofluoro-benzene by Kahane-Paillous & Leach (80). The near ultraviolet emission spectrum of tetralin is described by Bapat (81).

FREE RADICALS

The spectrum of the free methylene radical CH_2 has been observed by Herzberg & Shoosmith (82). It was obtained by the flash photolysis of diazomethane and examined with a 3m. vacuum spectrograph. The strongest features, occurring about 1415 A when examined under various degrees of deuteration, indicate the presence of two hydrogen atoms symmetrically placed. The absorption spectrum of HNO and DNO, obtained by the flash photolysis of nitromethane and other compounds, has been photographed under high resolution by Dalby (83). It is shown that the molecule is more bent in the excited state. The absorption spectra of trapped NH_2 radicals at 4.2°K. are described by Robinson & McCarty (84) and that of some active species by Rice & Ingalls (85). An extensive study of the electronic absorption spectra of NH_2 and ND_2 has been made by Dressler & Ramsay (3). The radical is bent in the ground state and is linear in the excited state. Further flash photolysis studies have been carried out on the NCO and NCS radicals (86) and indicate that the radicals are linear in both the ground and the excited states. A useful summary of the contributions made at an informal conference in Sheffield (Sept. 1958) is given by Porter (87). The free radicals produced by gamma radiolysis of aromatic solutions in rigid glasses have been identified by their absorption spectra and shown to be similar in most respects to those produced by ultraviolet photolysis (88). The spectra of many substituted aromatic radicals obtained by photolysis in EPA[2] glasses are given by Porter & Strachan (89).

[2] EPA—ether:isopentane:ethanol, in the proportion 5:5:2.

Singlet-Triplet Transitions

The upper limit of the 3400 A singlet-triplet absorption in oxygen-free benzene has been investigated by Craig, Hollas & King (90). No detectable absorption was present in paths of 22.5 m. of liquid, giving an upper limit to the oscillator strength of the transition of $f = 7 \times 10^{-12}$. Ferguson (91) has determined the relative quantum efficiencies of fluorescence and phosphorescence as a function of exciting wavelength for a number of aromatic compounds in solution or rigid glasses. Measurements of the temperature dependence of the fluorescence from crystals of tetracene and 9,10-dichloro-anthracene show that the quenching processes have activation energies of the order of the lattice vibration frequencies. Calculations of the lifetime of the phosphorescence of halogen-substituted naphthalenes have been made and compared with experimental results by Iguchi (92). The polarization of the phosphorescence of naphthalene and phenanthrene have been studied by Williams (93). These substances were dissolved in EPA glass at 77°K. and irradiated with plane-polarized exciting light sufficiently monochromatic to be absorbed by only a single electronic transition. The phosphorescence transition is perpendicular to the plane of the ring for phenanthrene and lies along the short axes for naphthalene. Comparison of the observed polarizations with those predicted for various assignments of the triplet level show that no assignment is possible in the case of phenanthrene. An assignment is possible in the case of naphthalene though there is some uncertainty because of possible contributions from vibrationally induced transitions. Kanda *et al.* (94, 95) discuss the low temperature triplet-singlet emission of toluene and phenanthrene. Absorption and luminescent spectra of aromatic crystals at 20°K. of normal and fully deuterated benzene and naphthalene have been reported by Zmerli (96). The very important demonstration by Hutchison & Mangum (97) of the paramagnetic resonance absorption in the phosphorescence state of naphthalene in solid solution in durene showed that this state is indeed a triplet.

Continuing his work on the enhancement of singlet-triplet transitions by oxygen under pressure, Evans (98) has measured the singlet-triplet bands of a number of monosubstituted benzenes and monoaza-aromatics. On comparing the shifts of the triplet with that of the lowest singlet the following generalizations can be made. If the substance does not have a multiple bond, the shift of the triplet is rather less than that of the singlet. If, a multiple bond is present, however, the reverse is generally true. Singlet-triplet bands have been observed with ethylene deutero-ethylene, butadiene, a number of conjugated olefines, diacetylenes, and a variety of substituted acetylenes. With butadiene and hexatriene, transitions to a second triplet level are observed. Conversely, ethylene and acetylene considerably perturb the Herzeberg $^3\Sigma_u^+ - ^3\Sigma_g^-$ bands of oxygen and increase their intensity.

Triplet-triplet spectra.—Porter & Windsor (99) report triplet-triplet spectra for 32 organic molecules, for ten of which absolute extinction coefficients and oscillator strengths have been found. Lifetimes have been measured for

naphthalene and anthracene in a wide variety of solvents. Stockburger & Schüler (78) have also observed these in absorption in gaseous discharges.

CHARGE-TRANSFER SPECTRA

Merrifield & Phillips (100) report the electronic (charge-transfer) spectra of the D-complexes of various aromatic molecules with tetracyanoethylene. The latter compound is a member of the "cyano-carbons" which contain only the cyano group attached to carbon. It is the strongest "π" acid yet examined. Looney & Downing (101) report the spectra of some "cyano-carbons" and their salt anions. Spectra of the α,β-ethylenic nitriles are given by Heilmann & Bonner (102). The wavelength shifts of the charge-transfer bands of 1-alkyl-pyridinium iodide complexes are correlated with solvent polarity and also with solvent parameters deduced from kinetic studies by Kosower (103). Booth, Dainton & Ivin (104) have made spectrophotometric studies of the 1:1 complexes of SO_2 with 8 olefins and several aromatic hydrocarbons. The results have been interpreted in terms of two distinct transitions, (1) charge-transfer absorption by the complex which gives rise to a band whose position varies with the ionization potential of the hydrocarbon and (2) an enhanced absorption of the SO_2 transition at 2960 A. Several charge-transfer spectra of inorganic and organic complexes have been measured by Drickamer & Stephens (105) as a function of pressure. The shifts of band peaks for inorganic compounds can be explained in terms of the effect of the pressure on the acceptor levels of the metal relative to the ligand levels. The large red shifts observed in the peaks for the organic complexes can be explained in terms of solid-state band theory. A pressure-induced ligand field peak in K_2ReCl_6 is reported by these workers.

Briegleb & Czekalia (106) have described a method of determining the ionization potential (Ip) of electron donors from the frequencies (ν) of the charge-transfer bands of the complexes with certain electron acceptors. This is based on a non-linear theoretical relationship between Ip and ν. Similar results have been obtained by Foster (107) from an empirical relation set up from complexes of donors having a reliably known Ip with standard acceptors. This method gives 7.8 ev for the Ip of hexamethyl benzene, which is in agreement with a direct photoionization measurement (108) of the vapour but 7.4 ev for aniline as against 7.70 ev reported for the vapour by Watanabe (109). It is possible that the relation could be applied to obtain the ionization potentials of large molecules that would be difficult to obtain in the gas phase.

Solvation spectra.—The effect of environmental changes upon the ultraviolet absorption of solvated iodide ions has been discussed by Smith & Symons (110). Shifts arising from changes in the solvent, from the addition of other ions and from temperature variation are interpreted in terms of a charge-transfer-to-solvent mechanism, the excited orbital being located in an oriented solvent cavity. The shift of the I^- absorption in alkali halide crystals on melting is a somewhat related phenomena. Rhodes & Ubbelohde

(111) investigating *inter alia* lithium iodide crystals show that the wavelength of maximum absorption shifts to longer wavelengths as the positional disorder increases with rise in temperature of the solid and on melting. Simultaneously, there is a decrease in intensity of this maximum. For crystals containing ions of a more complex shape, such as nitrates and thiocyanates, the formation of ionic complexes facilitate the melting.

Magnetic and spectrophotometric studies of the solutions of alkali and alkali earth metals in ammonia and other solvents have been reviewed by Symons (112). Generally one or two electronic absorption bands at 6700 and 15,000 cm.$^{-1}$ for sodium in ammonia cause the blue colour of the solutions, the former being always associated with paramagnetism and the latter being diamagnetic. Their behaviour seems to be best explained in terms of "solvent cavity" theory (113, 114).

The flash photolysis of halide salts in aqueous and alcoholic solutions yields unstable species believed to be the dihalide ion (I_2^-, Br_2^-, etc.), the absorption spectrum of which has been recorded by Edgecombe & Norrish (115). The interpretation they propose is based on the Rigg & Weiss mechanism of electron transfer which involves the postulation of the splitting of the solvent molecule (136, 137).

Carbonium and Other Organic Ions

Spectra of solutions of various carbinols and hydrocarbons in sulphuric acid, prepared according to certain special procedures, have been attributed to the appropriate carbonium ions by Grace & Symons (116). They include a number of monoaryl carbonium ions which are found to be surprisingly stable in dilute solutions in sulphuric acid in this group. Rosenbaum & Symons (117) have used the same procedures for the preparation of CMe_3^+ ions from t-butyl alcohol and 2,methyl propene. This is associated with a single ultraviolet absorption band at 292 mμ. Alkyl substituent and solvent effects in the principal ultraviolet transitions of some organic positive ions are discussed by Schubert *et al.* (118). Correlations between the electronic spectra of alternant hydrocarbons and their mono- and divalent ions are discussed by Hoytink (119) with special reference to benzene, coronene, and triphenylene. The electronic spectra of conjugated polyenes before and after protonation are reported by Wasserman (120).

'n − π' Transitions

In a series of papers on the electronic spectra of N-heteroaromatic systems, Mason (121) has reported studies on the n − π bands of the monocyclic azines, the substituted monocyclic azones, the 'π − π' transitions of the monocyclic hydroxy-azines, and the vibrational and rotational structure of the n − π band of sym-tetrazine. Vibrational and high resolution electronic spectral studies of 1,2,4,5-tetrazine are also reported by Spencer (122). Zanker & Schmid (123) report the electronic spectra (at −183°C.) of several types of N-heterocyclics including benz- and dibenzacridene isomers both as

bases and cations; the results are compared with the analogous polycyclic aromatic spectra and the transitions are classified. Theoretical calculations have been made by Goodman and co-workers (124, 125) on $n - \pi$ transition energies, etc. in N-heterocyclics. The interaction of certain polar solvents in particular nitriles and alcohols on the $n - \pi$ absorption of benzophenone has been investigated by Becker (126). Shifts to the violet in the electronic spectrum are accompanied by reductions in the carbonyl frequencies (infrared). The data indicate electrostatic interaction between the positive C atom of the nitrile group and the non-bonding electrons of the carbonyl oxygen.

HYDROGEN BONDING

The collected papers of the H-bonding conference held in Ljubljana in 1957 has now appeared (127) and contains many important articles on the experimental as well as the theoretical aspects of this subject. A book by Pimentel (128) is largely devoted to the spectroscopic aspects of the subject. Paolini (129) discusses the nature of the H-bond with reference to its effect on the OH stretching vibration, $n - \pi$ electronic transitions, and dipole moments. Forbes & Knight (130) report ultraviolet studies on the effect of solvent-solute interactions on the intermolecular hydrogen bond in benzoic acids.

EFFECT OF PRESSURE

Babb, Robinson & Robertson (131) have studied the effect of high pressure on the near ultraviolet spectra of benzene in a number of different diluent gases over a wide range of diluent densities. In general, the band systems are shifted to the red except when helium and neon are used as diluents. Dispersion theory predicts only roughly the relative shifts and does not explain at all the blue shifts. Robertson & King (132) present results on the shift of the absorption of benzene, naphthalene, pyrene, and phenanthrene with density of the diluents helium and nitrogen. They argue that the blue shifts in the benzene ^1L_b spectrum are caused by neither short range repulsive forces nor long range dispersive ones. It is assumed that weak, long range non-dispersive forces are present in the benzene-helium interaction that have the character of repulsive forces. Similar studies have been carried out by Oksengorn (133) using compressed N_2, Ar, He, H_2, CO, and CO_2 as mixtures with several aromatics. Frequency shifts proportional to pressure were observed, helium being the only gas that produced a short wavelength shift. He proposed a correlation of the magnitude of the shifts with the ionization potential of the aromatic used. The effect of pressure on the near ultraviolet spectra of some fused ring aromatic crystals has been reported by Wiederhorn & Drickamer (134). Other work of Drickamer and associates on pressure effects is reported in the section on charge-transfer spectra. Vodar (135) has reviewed the recent work at Bellevue on the effect of pressure on molecular electronic and infrared spectra. The report also includes data concerning the satellites that are observed in the electronic spectra of metallic vapours in a highly compressed foreign gas.

STERIC HINDRANCE

Steric effects in methyl substituted α,β unsaturated aldehydes are reported by Forbes & Shelton (147), who discuss the electronic spectra and molecular dimensions. The spectra of a large number of diaryl ethers, which reveal large steric effects due to ortho-substituents, are reported by Dahlard & Brewster (148). Several new hindered diphenyls are discussed by Beaven & Johnson (149) and Marcus *et al.* (150).

ORGANIC CRYSTALS

The excellent reviews on this subject by McClure (12) and Wolf (11) have already been mentioned. Schnepp, Kopelmann & McClure (151) report the spectra of 1,3,5-trichloro- and hexachlorobenzenes, and of durene in the crystalline state, and discuss transition polarizations in relation to crystal and molecular symmetry. Absorption and fluorescence spectra have been obtained by Wolf (152) at 77°K. for hexamethyl benzene with polarized light travelling perpendicular to the *bc* plane. There are two modifications, one stable and the other metastable, below 110°K. which are thought to differ by a switch in position of the CH_3 groups. Spectra of a number of pure aromatic crystals are reported by Pesteil & Ciais (153). Detailed studies of the absorption of anthracene crystals in plane-polarized light at temperatures 295, 90, and 4°K. have been made by Lyons & Morris (154). Zmerli & Poulet (155) ascribe some of the absorption and luminescence lines in the spectrum of benzene, naphthalene, and their fully deuterated analogues at 20°K. to exciton transitions. Craig & Walsh (156) have given a theoretical treatment of the crystal spectra of benzene and naphthalene. The results of the analysis of the crystal spectrum of naphthalene have been compared with those of the vapour, for which analysis was made possible by calculating the expected rotational envelopes of the bands. Bands that derive their intensities by vibrational perturbation show doubled heads and calculations show that these are associated with short-axis transitions. The calculations for long-axis transitions lead to the expectation of single headed bands associated with the allowed transitions. It was thus possible to assign the allowed bands to B_{2u}—A_g and the vibrationally induced bands to B_{1u}—A_g solely on the evidence from the vapour spectrum (157, 158). Polarized spectra of single crystals of paradichlorobenzene are reported by Sirkar & Misra (159). The identical positions of some of the $0 \rightarrow v$ bands in spectra with the **E** vector parallel to the *b* axis and to the *c* axis indicate that there is no Davydov splitting in this crystal, though a calculated expected value of 22 cm.$^{-1}$ should have been easily observed.

INORGANIC CRYSTALS

In view of the extensive article by McClure (13) on the spectra of ions in crystals, only brief mention of this topic will be made. The electronic spectrum of the nitrate ion has been investigated by Friend & Lyons (160). That of a single crystal of manganous fluoride has been measured in the range 2700 to 6000 A and down to 20°K. by Stout (161). The ultraviolet ab-

sorption of molten and solidified mixed salt systems $NaNO_2$—$NaNO_3$ and $NaCl$—$CdCl_2$ have been reported by Sakai (162) and that of $NiCl_2$ in molten $LiCl/KCl$ by Sundheim & Harrington (163). Studies of changes in the spectra of ionic crystals when melted have already been mentioned (111). Detailed electron-spin resonance studies of MnO_4^{2-}, MnO_4^{3-}, and FeO_4^{2-} by Symons (164) show that the unpaired electrons are in a doubly degenerate level and not in a triplet level as assumed in the earlier analysis (165).

Biological Topics

An important paper by Karreman & Steele (166) discusses the long range transfer of electronic energy in biological systems by a resonance mechanism. Many papers of importance in this connection are to be found in the *Discussions of the Faraday Society* article on "Energy Transfer in Biological Systems" (167). Fernandez & Becker (168) have shown that dry chlorophylls *a* and *b* in a rigid glass hydrocarbon solvent have intense emission at 7550 and 7330 A respectively. In each case the room temperature absorption shows a long wavelength shoulder on the main red band. Both the absorption and the emission disappear in the presence of hydroxylic solvents and are interpreted as $n-\pi^*$ singlet and $n-\pi^*$ triplet transitions respectively; lifetimes are estimated. The effect of pH on the fluorescence of tyrosine, tryptophan, and related compounds are discussed by White (169). Teale & Weber (170) discuss the polarization of the ultraviolet fluorescence of proteins. Birks & Cameron (171) report the fluorescent spectra of 41 organic compounds, including known carcinogens and related structures, as excited by Hg 2537 in the microcrystalline state. Several classes of spectra are discussed in relation to various degrees of molecular interaction in the lattice. Karr (172) lists, in order of increasing wavelengths, the bands of longest wavelength in the ultraviolet spectra of 408 polycyclic aromatic hydrocarbons. These can often be used for purposes of identification. The absorption of thin films of aromatic compounds is reported by Perkampus (173). Smellie (174) reports changes in the ultraviolet absorption of trypsin with the disruption of tertiary structure. The fluorescence of tryptophan derivatives in trifluoroacetic acid has been described (175) as has that of amino acids in aqueous solution (176). The far ultraviolet absorption spectra, down to 1750 A of steroids and triterpenoids, has been investigated by Turner (177).

Miscellaneous

The ultraviolet and visible absorption spectra of aromatic amines absorbed on specific centers of aluminum silicate catalysts have been described by Kotov & Terenin (178). A method has been devised by Labhart (179) for obtaining the directions of transition moments of molecules in which the dipole moment coincides with the symmetry axis. The molecules are oriented in a strong pulsating electric field and the variation of the extinction coefficients for radiation polarized parallel to the field is measured. The phototropic properties of a crystal of 2-(2,4-dinitrobenzyl) pyridine have been

studied using polarized radiation by Clark & Lothian (180). The activation energy of the bleaching process has been found and the results suggest that the coloration is associated with the transfer of a hydrogen atom from the CH_2 to the N atom during a bending vibration of this group.

Interferometric techniques have been applied to the resolution of the rotational structure of polyatomic molecules. Poole, Raynes & Stace (181) used a quartz Lummer plate on the absorption spectrum of formaldehyde vapour in the region 3250 A and obtained a resolution better than 0.1 cm.$^{-1}$ with an accuracy of about 0.003 cm.$^{-1}$ over a range of 2000 cm.$^{-1}$ from a single plate exposed for only 10 min. The reduction of the plate was greatly simplified by use of an electronic computor. Similar work had previously been carried out by Kadesch, Moldenhauer & Winans (182) using a Fabry-Perot interferometer. The rotational lines of thallous chloride were measured with an accuracy of 0.01 cm^{-1}.

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DIELECTRIC POLARIZATION AND LOSS[1]

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The subject of dielectric behavior has not previously been dealt with as such in these reviews, although dielectric properties relevant to other subjects have often been mentioned. There have, however, been a number of comparatively recent books and review articles on various aspects of dielectrics. In organizing the present discussion, it has seemed worth-while to mention first the more generally useful references with brief comments on their content and approach, and then to outline some of the more recent lines of significant developments, inserting references to review articles on special aspects at the appropriate places.

LITERATURE SOURCES

Beginning in 1949, a series of books has been produced to fill the needs for more up-to-date monographs than the classic *Polar Molecules* by Debye, and *Dielectric Constant and Molecular Structure* by Smyth. Fröhlich's *Theory of Dielectrics* (1) is devoted principally to treatments of molecular interaction effects by classical statistical mechanics; Böttcher's *Theory of Electric Polarisation* (2) has a thorough discussion of classical electrostatic theory and its application together with elementary statistical mechanics to dielectrics problems. A long monograph by Brown (3), also largely theoretical, gives an excellent critical account that begins with fundamental principles and includes illustrative applications. The treatment is particularly valuable for clarifying the approximations and simplifying the assumptions of current theories.

The monographs just mentioned are nicely complemented by Smyth's *Dielectric Behavior and Structure* (4), which briefly presents principal theoretical developments and gives a very full account of the dielectric constant and loss measurements on a wide variety of gases, liquids, and solids, together with detailed discussions of dipole moments in relation to molecular structure. The latter aspect of the subject is also treated at length in Smith's *Electric Dipole Moments* (5) and more briefly by LeFèvre (6) in a monograph of the Methuen series.

All the books mentioned in the preceding paragraph contain some discussions of experimental methods, with references to other sources. There are, of course, many texts on electrical currents and techniques with material relevant to dielectric studies, but no particular reference can be singled out as a uniquely useful or complete account of currently available methods.

Collectively, the general references so far cited quite adequately cover the principal developments to 1956. More recent results can, for the most

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[1] The survey of literature was completed December 1959.

part, only be found in the original papers, but there is a valuable index of
these which is not as widely known as it should be. This source is the annual
Digest of the Literature on Dielectrics (7). The most useful chapters for sub-
jects of physical chemical interest are on "Molecular and Ionic Interactions
in Dielectrics," with some 150 to 300 references yearly in recent issues,
"Tables of Dielectric Constants, Dipole Moments and Dielectric Relaxation
Times," averaging about 100 references; and "Instrumentation and Measure-
ments," with more than 250 references. The tabulations and capsule de-
scriptions necessarily give less information than abstracts, but they are in-
valuable guides to literature sources.

THEORETICAL DEVELOPMENTS

Several recent papers have dealt with two basic aspects of dielectric the-
ory: the form in which measurable macroscopic quantities are expressed
as averages over molecular charge distributions, and the constitutive rela-
tions for macroscopic displacement D, field intensity E, and polarization P.
Lorentz, in his classic discussion of the molecular field equations, related
them to the macroscopic Maxwell equations by not very specifically defined
space-time averages over the macroscopic quantities. Mazur & Nijboer (8)
have recast these in terms of charge and multipole moment densities ob-
tained by classical statistical mechanical ensemble averages; Jansen (9)
has explicitly introduced quantum mechanical expectation values for molec-
ular multipole moments prior to ensemble averaging to the governing equa-
tions for D, E, P, and their magnetic counterparts.

These results provide a more satisfactory formal connection between
electromagnetic theory and statistical and quantum evaluation of equi-
librium properties in molecular terms than earlier treatments; they also show
the approximate character of the usually accepted Maxwell relations div
$D = 4\pi\rho$ together with $D = E + 4\pi P$. Thus, if D is required to satisfy the
former equation with charge density ρ expressed as an ensemble average,
then the constitutive relation for D is of the form $D = E + 4\pi(P - \text{div } Q$
$+$ higher multipole terms); where Q refers to the macroscopic quadrupole
moment tensor and the vector div Q has cartesian components of the form
(div $Q)_x = \partial Q_{xx}/\partial_x + \partial Q_{xy}/\partial_y + \partial Q_{xz}/\partial_z$. Significant contributions of the div Q
term can ordinarily be produced only by much more strongly inhomogene-
ous macroscopic fields than are ordinarily feasible, but the modified expres-
sion could conceivably be put to use in special circumstances for a study of
molecular quadrupole moments. (Quadrupole effects of other kinds are dis-
cussed below.)

Another subject of recent investigations has been the question of the
validity of representing induced moments of molecules as the product of
electric field and a polarizability α which is regarded as a molecular constant.
The questions treated are not the quantum significance of the term for iso-
lated molecules in small external fields, but rather what modifications result
if there are strong fields of external charges or strong and inhomogeneous
fields of neighboring molecules.

Jansen & Mazur (10) and later Jansen & Solem (11) have examined the quantum for pair interactions of noble gas atoms and single molecules; they find no change in polarizability in an external field in first and second order perturbation calculations, but a small increase from third order terms. The calculated effect on dielectric constants of imperfect non-polar gases, using quite approximate wave functions, amounts only to a fraction of a per cent at pressures of 100 atm. Buckingham (12) has discussed the problem in terms of an added "hyperpolarizability" term proportional to the cube of field strength at the molecules, whether resulting from fields of external charges or of interacting neighbors. Jansen (9) has pointed out that the quantum mechanical problem of pair interactions cannot strictly be represented by the concept using an intermolecular field, but Buckingham has found that predicted effects by the two methods are not very different for hydrogen atoms.

The pair-interaction calculations can only be expected to represent observable effects at rather low densities of imperfect gases; the limited experimental evidence under these conditions is discussed later. It is of interest to recall the quite different approach of de Groot & Ten Seldam (13), who calculated the change in polarizability of "caged" atoms by requiring that their wave functions vanish at a finite distance from the nucleus and found significantly decreased polarizabilities for this model. The quantitative value of the approach for representing polarization effects at dense gas or liquid molecule concentrations is dubious, but the fact that deviations are predicted by this and other models shows the dangers of accepting constant scalar or tensor polarizabilities as an exact basis for calculations of induced moments and polarizations of interacting molecules.

Finally, a variety of studies have used molecular quadrupole moments to represent effects of short range molecular interactions to the next degree of approximation after ionic and dipole moment terms. These multipole moment sums for nuclei and electrons (not to be confused with nuclear quadrupole moments for charge distribution of nuclei) can, for molecules with a z axis of symmetry, be expressed in terms of a single sum $\theta = \Sigma_i e_i (z_i^2 - x_i^2)$ over charges e_i at distances x_i from this axis, and by two similar sums for molecules of lower symmetry. The application of most direct significance for dielectric properties was the independent prediction by Zwanzig (14) and by Buckingham & Pople (15) of a quadrupole-induced dipole contribution of a pair of molecules to dielectric constants of imperfect polar gases. The effect, produced by the net quadrupole field of a neighboring polarized molecule, is considered further in the next section.

Several applications of quadrupole interactions to interpreting quite different physical effects should be mentioned in passing. Thus, Pople (16) and Buckingham (17) accounted for the equation of state and heat of sublimation of CO_2 in terms of quadrupole attractive forces, finding values $\theta = 5.7 \times 10^{-26}$ and 5.3×10^{-26} e.s.u. cm.^{2} to fit the measurements, while Lupton (18) has shown that the considerable differences in heats of sublimation and solid phase transitions of N_2 and CO can result from a larger quadrupole moment

of the latter (the permanent dipole effect being much too small). The highest order explanation of this kind to date is undoubtedly the treatment of CD_4 by James & Keenan (19) in terms of octupole-octupole interactions. In still a different area, Buckingham (20) has suggested that differences in heats of solvation of atoms, anions, and cations in water may be attributable to the opposite sign of ion-quadrupole interaction energies for the solvated water molecules; the necessary quadrupole moment of order 3.9×10^{-26} e.s.u. is, however, much larger than point charge models would suggest. Another example is Kington & Macleod's (21) correlation of differential sorption heats of O_2, N_2, CO, CO_2 on chabazite with values of quadrupole moments deduced from microwave broadening.

These diverse uses of quadrupole terms to represent short range interactions indicate the importance of quadrupole moment measurements; such values should also give important information about electron charge distribution in molecules. Unfortunately, the quantity is an elusive one experimentally, as molecular effects are normally accompanied by a variety of others of uncertain magnitude, and more direct determinations require strongly inhomogeneous macroscopic fields to produce even small effects. An interesting possibility, apparently first suggested by Debye (22) and recently discussed in detail by Buckingham (23), involves use of the inhomogeneous field near the axis of four rods that form a square array in cross section, opposite pairs being at positive and negative potentials. If the slight orientations of quadrupoles in this region give rise to sufficient optical anisotropy of polarizability, measurements of the Stark-effect refractive index difference should give the magnitude and sign of the quadrupole moment. It can be hoped that the purpose of the ingenious method will not be defeated by the smallness of the effect.

DIELECTRIC BEHAVIOR OF GASES

Both the equilibrium and dispersion effects in dilute gases are principally of interest in helping to elucidate molecular structures or in testing theories of molecules which are, except for infrequent collisions, independent; these aspects are taken to be outside the scope of this review. A few recent publications in this area should, however, be mentioned.

First is an extensive critical tabulation of dielectric constant and dipole moment data prior to 1933 for some 350 gases by Maryott & Buckley (24). This, together with the annual compilations in reference (7), is a good starting point in a search for such information about a particular molecule.

A topic of recent interest is the observation and interpretation of nonresonant absorption by such polar gases as CH_3Cl, CH_3CN, and $CHFCl_2$, usually in the microwave region. Here the absorption is by transitions between states of virtually zero energy difference, the sharp resonance lines of conventional microwave spectroscopy being replaced by broad absorption regions of the Debye relaxation type. Several series of investigations, principally by Birnbaum and co-workers for dispersion (25), and by Boggs and

co-workers (26, 26a) for absorption, have established such relaxation behavior for a number of simple molecules.

The term "inversion" has been used to describe the dipole moment changes responsible for non-resonant absorption; the unfortunate implication that a tautomerism or ammonia-like inversion is necessary for the effect has aroused undeserved suspicion of it. Wilson (27) has shown that the seeming difficulty is one of terminology and disappears when the distinction between wave functions of unlike symmetry with non-vanishing dipole moment matrix elements connecting them, and wave functions corresponding to physical inversion is recognized. Satisfactory agreement between experimental magnitudes of dispersion and theoretical rigid rotor treatments has been found in the references cited, and the relaxation frequencies are essentially those expected from collision models.

The static dielectric constants of imperfect gases at moderate densities have been the subject of a considerable number of theoretical treatments, especially for non-polar gases. The elementary theory of non-interacting molecules, or of weak interactions in special cases, predicts that the Clausius-Mossotti function $(\epsilon-1)/(\epsilon+2)(N/V)$ for dielectric constant ϵ as a function of molar density N/V (moles/cm.³ or moles/liter) should depend only on molecular constants and temperature. Molecular pair and higher order interactions, however, make density-dependent contributions represented in a virial-type treatment by a series expansion in density of the form

$$(\epsilon - 1)/(\epsilon + 2)(N/V) = A + B(N/V) + C(N/V)^2 + \cdots$$

The coefficient A is $(4\pi N_o/3V)(\alpha+\mu^2/3kT)$ for the model of molecules with mean polarizability α and permanent moment μ, N_o being Avogadro's number; the coefficients $B, C, \cdots$ are second and higher "dielectric virial coefficients" from pair, triplet, and higher order interactions.

Of the various treatments of the coefficient B for non-polar gases, those of Jansen (9) are the most complete. For rare gas atoms and the molecules N_2, CO, and CO_2, Jansen has calculated contributions from transitional fluctuations, change in effective polarizability, and quadrupole-induced dipole moments. The predicted increases are smaller than experimental uncertainties in most of the experimental measurements of the very small changes in dielectric constants for the relevant pressures of tens of atmospheres at most.

Experimentally, Oudemans & Cole (28) have found virtually zero values of B for helium and argon. In CO_2, an appreciable density effect clearly exists [Keyes & Oncley (29); Michels & Kleerekoper (30)], such that B is positive, but the magnitude is not yet well defined. The corresponding Lorenz-Lorentz function $(n^2-1)/(n^2+2)(N/V)$ for refractive index n shows little if any increase in the same range, and the difference has been shown by Buckingham (31) and Jansen (9) to be of the order expected for the quadrupole interaction effect.

The Lorenz-Lorentz function would be expected not to show any orienta-

tion-dependent effects, and so has fewer contributing causes to a variation with density than has the Clausius-Mossotti function. By assuming that the Lorenz-Lorentz function (often called the molar refraction) is strictly independent of density, Ashton & Guggenheim (32) have calculated gas densities from measured refractive indices, and by simultaneous pressure measurements have obtained very satisfactory imperfect gas equations of state data without direct density determinations. The method is attractive, but available data are too meager to show very clearly how far the underlying assumption can be trusted.

Triplet fluctuation effects contributing to the coefficient C in the dielectric constant function have been examined by de Boer, Van der Maesen & Ten Seldam (33), using products of pair-distribution functions for the averaging. Because of this approximation, the results are of uncertain accuracy, but the predicted negative values of C are in agreement with observed decreases of the Clausius-Mossotti function at higher gas densities.

For polar gases, much less has been attempted. Buckingham & Pople (34) have calculated pair effects from dipole moment and polarizability interactions using somewhat different assumptions from those made by Van Vleck (35) in his earlier treatment. The positive values of B predicted are considerably larger than those observed for ammonia (29). About the only other data for comparison are for fluoromethane, CH_3F, which shows decreases of the CM function at pressures above 20 atm.; Buckingham and Pople suggest shape-dependent repulsive effects favoring anti-parallel dipoles at short range as a possible cause.

Evidently all these aspects of compressed gas behavior are in a rather uncertain state. Much experimental work is needed to clarify the situation, but there are already grounds to permit suspicion of the quantitative adequacy of current theories.

Frequency-dependent effects have been examined in several connections. The transition from broadening of resonant microwave absorption lines to typically relaxation absorption at high densities as inertial effects are suppressed has been treated theoretically in some detail by Gross & Lebowitz (36) and by Sack (37). Phillips (38) some time ago reported microwave dielectric constant and loss values at pressures to 600 atm. for $CHCLF_2$ and N_2O; considerable and varied effects were found, but interpretations were very uncertain because only values at the single wavelength of 1.22 cm. could be obtained. Birnbaum, Maryott & Wacker (39) found microwave absorption in CO_2 proportional to the square of gas density, and suggested relaxation of the quadrupole interaction as the origin. In such problems also, much experimental work and development of theory will doubtless be needed to define the effects adequately, but interesting possibilities for extracting useful molecular quantities and transport properties may then be realized. The appearance of recent papers on the construction of pressured waveguide equipment [cf. Lawson & Smith (40)] suggests that more experimental results may be forthcoming.

Dielectric Constants of Liquids and Solutions

The static dielectric constants of liquids appear as parameters in a variety of theories regarding liquid and electrolyte behavior, and accurate values are obviously important for many purposes. A critical tabulation of literature values prior to 1951 for more than 800 pure liquids has been given by Maryott & Smith (41); more recent data are accessible by the annual tabulations in reference (7). Comments on values for a few particular substances are appropriate here because of their special importance.

The dielectric constant of water has been determined at or near room temperatures by a host of workers, and over wider ranges in a number of investigations, with disagreements approaching a per cent or more, even in the seemingly more reliable values. This somewhat surprising situation is principally attributable to the significant conductivity of even the purest water, which gives rise to residual errors or insensitivity in the experimental methods used. For a long time, the values of Wyman & Ingalls (42) obtained by Wyman's resonator method were usually adopted, but more recently Malmberg & Maryott (43) have reported results from a very thorough series of bridge measurements at audio and radio frequencies that are about 0.3 per cent lower over the range 0–100°C. The latter authors discuss the various experimental problems in detail, and to this reviewer seem to have made a good case for their values; some independent confirmation would, however, doubtless relieve the minds of electrochemists needing accurate values.

Reference liquids with accurately known dielectric constants are often useful for test and calibration purposes, and a number of investigators have put considerable effort into determining such standard values. Benzene is often used, although it is not ideal because of difficulty in removing traces of water; Hartshorn, Perry & Essen (44) found $\epsilon = 2.2836$ at 20°C., and Mecke & Rosswog (45) gave $\epsilon = 2.2826$. The latter authors give values for a number of other liquids, both polar and non-polar, as does Lafontaine (46). De Vos (47) has also given results of careful investigations for several liquids; he found CCl_4 to be poor because of impurities not easily removed.

A great number and variety of papers have appeared in the last several years on the theory of the dielectric constant of polar liquids and polar molecules in non-polar solvents. Many of these deal with elaborations and extensions of the theories of Onsager and Kirkwood, which made the first fundamental progress in remedying the well known deficiencies of the Lorentz field for condensed phases containing polar molecules.

Onsager's treatment (48) of polar liquids was based on electrostatic calculation of fields acting at an isotropically polarizable point dipole in the center of a spherical cavity, with surroundings represented by a continuum with the macroscopic dielectric constant. The result is in fair average agreement with experiment, as judged, for example, by comparison of dipole moments calculated from dielectric constants of pure polar liquids with those obtained from gas or dilute solution measurements if the liquid is not

obviously "associated" from other physical evidence. However, individual deviations of 10 to 20 per cent in either direction are fairly common, and a number of writers have introduced elaborations of Onsager's model which include anisotropy of the molecular polarizability, eccentric position of the dipole in its cavity, and ellipsoidal cavities as a better simulation of molecular shape.

Before outlining some of these developments, a sometimes overlooked approximation in Onsager's final formula as it is often employed should be mentioned. This is the replacement of the sum of molecular cavity volumes by the total liquid or solution volume, which simplifies the formulas and has no major effect at ordinary liquid densities, but for only moderate density changes this approximation gives results significantly different from those of the formula with a more realistic fixed cavity size. The formulas in question are given and discussed by Brown (3) who has also given a detailed critique of the Onsager approach.

For pure polar liquids, Abbott & Bolton (49) developed a modified formula based on a spheroidal cavity with dipole parallel to the symmetry axis; for prolate ellipsoids an increased dielectric constant is predicted, but for oblate ellipsoids the opposite is true. Buckley & Maryott (50) have applied similar formulas (without the cavity volume assumption) to more than 30 polar liquids and found considerable improvement in most, but not all, cases on using spheroidal shapes not far from what is estimated on geometrical grounds.

If an eccentric dipole position is assumed in the model, still other parameters result in the dipole treatment. Ferchmin (51) has gone even farther by calculating the effect of the inhomogeneous reaction field thereby produced at the molecule in orienting its quadrupole moment. The result for an anisotropically polarizable molecule is a net polarization proportional to the product of polarizability, dipole, and quadrupole moments, and to the eccentricity of the dipole position. Neither this effect nor the effect of the reaction field of the quadrupole itself can be calculated because of a lack of quadrupole moment data, but Ferchmin estimates that the contributions could amount to as much as 20 per cent of the dipole term.

Somewhere in such proliferation of correction terms, one may well begin to question whether the treatments are warranted for a model in which even the immediate neighbors of a molecule are represented by a macroscopic continuum. It does seem clear that the deficiencies of the spherical cavity and isotropically polarizable point dipole of the original Onsager model are usually reduced by introducing simple shape-dependent effects, but more elaborate treatments are probably better considered in Kirkwood's approach, which permits specific representation of near neighbor interactions.

Modifications of Onsager's treatment have been applied to solutions of polar molecules in non-polar solvents by Scholte (52) and by Ross & Sack (53), the objective being to find a better basis for dipole moment evaluations from solution data than provided by the Debye-Lorentz field treatment

which gives rise to erroneous calculated dipole moments—the so-called solvent effect. Here again there is some measure of success when anisotropy of polarizability and molecular shape are introduced in the Onsager approach, but neither treatment is wholly satisfactory. Brown (3) and Smyth (4) have reviewed these and other treatments in terms of the types of assumptions made and degree of agreement with experimental data.

More recently, Buckingham (54) has started with a statistical formulation patterned after Kirkwood's theory of polar liquids, and after using the cavity model for evaluating all neighbor interactions, obtained Ross and Sack's result. The calculation was prompted by a development of Harris & Brush (55), which was the counterpart for solutions of Harris & Alder's treatment (56) of polar liquids (see below) and gave a considerably different formula. Neither these, nor a variety of partly or wholly empirical solution formulas, usually with Debye's original Lorentz field model in the background, are wholly satisfactory. The only solvent for obtaining dipole moments which can surely be trusted to better than a few per cent is still a vacuum; this is not to say, however, that relative values or differences for similar molecules may not be more reliable than the absolute values.

Kirkwood's original theory of the dielectric constant of polar molecules was a major advance because it was based on the formalism of classical statistical mechanics from the beginning, evaluated long range dipole effects by electrostatic equilibrium arguments, and provided a means of introducing specific calculations of short range molecular interaction. A difficulty in the development was that induced polarization effects were taken into account somewhat incidentally at the end by an approximate local field argument not really consistent with the main treatment.

Harris & Alder's revision (56) of the Kirkwood argument to include polarizability effects in the formalism from the beginning led to a formula giving dielectric constants some 30 per cent larger than Kirkwood's result or Onsager's formula as a limiting case for a continuous model. Their paper led to a series of a dozen or more papers in rebuttal, which agreed in finding results equivalent or much more similar to those of Kirkwood and Onsager, but differed in their explanations of the reasons. The most satisfactory of these papers to the writer is Buckingham's observation (57) that one may not legitimately evaluate the mean moment of a sample when the total moment of a representative molecule is fixed if part of the resultant fixed moment is due to polarizability of the molecule in the resultant field of its neighbors. Kirkwood used this device essentially for permanent dipoles, but it fails for polarizable ones because the constraint on coordinates of other molecules, imposed by requiring that their resultant field be fixed, prevents use of macroscopic results valid for unrestricted averaging. A closely related problem is proper formulation of the internal energy of a system of interacting polarizable dipoles; this has been discussed in detail by Mandel & Mazur (58), see also Brown (59).

Buckingham developed a modified approach in which the device was

used only for a fixed permanent moment, and obtained a modified form of Kirkwood's result reducing to Onsager's formula for his model. Cole (60) represented induced moments explicitly by harmonic oscillators; in the absence of fluctuation effects this model gives essentially Buckingham's result, and for non-polar molecules it gives the Clausius-Mossotti expression. Fröhlich (61) treated the problem more macroscopically, representing the induced polarization by a continuum of "high frequency" dielectric constant ϵ_∞; his result corresponds to the ones just mentioned for the appropriate relations of ϵ_∞ to polarizability α. Other discussions have been given by O'Dwyer (62) and by Scaife (63).

All the methods of calculation utilize some form of simplifying approximations to obtain usable results, none of which are exact. However, the essential agreement on the form of equation embodying long-range effects gives a reasonably firm basis on which to examine models of short range interactions and to make at least semi-quantitative predictions. Simple models of strong specific interactions have been quite successful for water [Kirkwood (64), Pople (65)], aliphatic alcohols [Oster & Kirkwood (66), Dannhauser & Cole (67)], and liquid HF and HCN [Cole (68)]; it seems likely that similar approaches can be profitably applied to other substances.

DIELECTRIC LOSS IN LIQUIDS AND SOLUTIONS

The characteristic times for polar molecules in liquids to approach equilibrium with an applied electric field are of order 10^{-9} to 10^{-12} sec. at room temperature for molecules of moderate size, but can be in the microsecond range for large molecules and as long as milliseconds or seconds at sufficiently low temperatures. The study of reasonably simple polar liquids at ordinary temperatures has developed enormously in the last fifteen years because of the availability of better ultrahigh frequency and microwave techniques, and the general character of dispersion and absorption behavior has been reasonably well defined for a considerable number and variety of liquids.

An extensive compilation by Buckley & Maryott (69) gives data for about 200 polar liquids and for more than 150 polar molecules in dilute solution with aqueous and non-aqueous solvents. The tables list limiting static and high frequency dielectric constants (ϵ_0 and ϵ_∞), characteristic wavelengths of the absorption region or regions, and where necessary parameters characterizing the width in frequency, or wavelength, of the absorption region. In addition, graphical data are given for a number of substances, either as representative examples or because the data are not readily described by a few parameters. The general references cited earlier discuss dielectric relaxation effects; two reviews of dielectric absorption, Davies (70) and Dryden & Meakins (71), should also be mentioned.

The simplest observed frequency dependence of relaxation dispersion and loss is given by the complex dielectric constant expression $\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + i\omega T)$; where ω is radian frequency and T is the macroscopic relaxation time. This formula is commonly referred to as the Debye

equation because it resulted from Debye's classic model of relaxation in liquids, but the same frequency dependence is predicted by other theories and by any model for which the equations expressing the time dependence of polarization are the counterpart of simple first order kinetics. Agreement in this respect with observed behavior then merely justifies further analysis of the measured parameters ϵ_0, ϵ_∞, and T in terms of predictions made by various theories.

The frequency behavior of a considerable number of polar liquids at ordinary temperatures is quite well represented by the Debye equations, and much of the analysis of this behavior has been based on Debye's molecular model or modifications of it. Two distinct questions are involved in such analysis: the legitimacy of the Lorentz molecular field assumed by Debye, and the extent to which molecules actually reorient by a rotational diffusion type process which can be represented in terms of macroscopic viscosity concepts.

The macroscopic relaxation time T, in the Debye theory, is not equal to the time τ characteristic of molecular reorientations. Instead, the relation $T = [(\epsilon_0 + 2)/(\epsilon_\infty + 2)]\tau$ results from the Lorentz field assumption, and is hence suspect for polar media. Miller & Smyth (72) have compared values of T for different polar molecules of comparable size, or for the same molecule in different environments. They conclude that T and τ are much more nearly equal than would be expected from the Debye relation, and that a reasonably consistent correlation results from using the relation $T = [3\epsilon_0/(2\epsilon_0 + \epsilon_\infty)]\tau$ proposed by Powles (73).

The crudest theoretical approach to this question [Cole (74), Bolton (75)] was based on generalizing Onsager's equilibrium model by assuming that a relaxation function $(1 + i\omega\tau)^{-1}$ could be applied to molecular reorientations in the Onsager cavity and that reaction fields could be expressed in terms of the complex dielectric constant ϵ^* rather than the static dielectric constant used in the equilibrium theory. The dispersion equation derived from these assumptions gives roughly Debye curves with $T \simeq \tau$ and Onsager's equilibrium result as a limiting case. Because the equation is quadratic in ϵ^*, it has the unfortunate feature pointed out by Powles (73) and Schrama (76) that ϵ^* itself cannot formally be represented even by a linear superposition of simple relaxation functions. To avoid this, Powles empirically modified the cavity-and-reaction-field expressions in terms of ϵ^* in such a way as to give a linear equation with the result given above for the relation between T and τ. O'Dwyer & Sack (77) started from a more fundamental analysis of the Onsager cavity field and fluctuating reaction field for a special model of possible dipole orientations; this gave the Powles result as a first approximation and more complicated further terms as the beginning of a series of doubtful convergence.

A formulation of the problem reducing to Kirkwood's equilibrium theory as a special case has very recently been given by Glarum (78), using Kubo's statistical treatment of irreversible processes (79). This gives a linear formal connection between observed macroscopic and molecular relaxation func-

tions. For rigid dipoles, a single macroscopic relaxation function is related to the molecular one by $T = [3\epsilon_0/(2\epsilon_0+1)]\tau$, while a somewhat artificial introduction of induced polarization as an instantaneously relaxing polarization gives Powles' result. To the extent that these various predictions can be trusted, the ratio T/τ for simple relaxation processes must lie between 1 and 1.5 at most; the implication then is that for many comparison purposes the difference between T and τ is unimportant, especially when exponentially varying effects of temperature are considered.

Debye related his rotational diffusion constant, and hence τ, to the macroscopic liquid or solution viscosity η by the Stokes hydrodynamic result applied to a sphere of molecular volume V, obtaining the equation $\tau = 3\eta V /kT$. Meakins (80) has compared measured values of T for large polar solute molecules in different non-polar solvents with values of τ calculated using volumes V from molecular dimensions, and found reasonably good agreement in cases where solute molecule volumes were more than three times those of solvent molecules.

At the opposite extreme, many workers have found relaxation times much shorter than the predicted values if the solute molecules are large, and Smyth and co-workers (81, 82) have found that unusually short or long relaxation times (as judged by comparison with $\tau = 3\eta V/kT$) can often be correlated fairly well with dipole moments being parallel to short or long axes of the molecules. The latter types of behavior can be accommodated to some extent in the viscosity model by Perrin's treatment of an ellipsoidal molecule with dipole moment components along the principal axes; Oncley (83) has used this type of approach to interpret relaxation of protein molecules in solution.

Many observed relaxation times in solution or in pure polar liquids can only be reconciled with the Debye approach by assuming an effective "microscopic viscosity." Hill (84) has developed a theory of solution viscosity based on Andrade's momentum transfer model and has deduced an expression for a "mutual viscosity" characteristic of the interaction of solute and solvent molecules in terms of the viscosity of pure solute and solvent. Use of this modified viscosity in the expression for τ gave improved agreement in a number of cases, and Pitt & Smyth (85) have developed a modified formula not involving pure solute viscosity which they have applied with fair success to a variety of solution measurements.

All the foregoing treatments retain in some degree the concept of molecular reorientation as a diffusion process of many infinitesimal jumps; the picture has been questioned by several writers who argue that less frequent large jumps, made possible by fluctuation of the molecular environment, are a more realistic description of the actual motions. On this basis, the success of Debye's expression results from introducing macroscopic viscosity to evaluate the diffusion mechanism; the further argument is that the parallelism often found between viscosity and relaxation times, neither of which proceeds by accumulation of small fluctuations in molecular positions, is better attributed to the similarity of the underlying molecular process.

This viewpoint was advanced by Kauzmann (86) for the dielectric problem, and recently a number of writers have developed models of diffusion or relaxation which involve formation of holes by cooperative interactions that permit discrete jumps in position or orientation. Thus, Beuche (87) has calculated the average frequency with which a critical expansion of volume around a molecule occurs as a result of coupled radial displacements of surrounding shells of molecules, while Cohen & Turnbull (88) have developed a free volume theory in which the probability of a localized critical excess volume is used to calculate the frequency of molecular jumps to new positions thus made available. Both treatments thus interpret the behavior in quite general physical terms rather than by specific molecular properties.

These treatments are of particular interest in connection with the observed temperature dependence of dielectric and other relaxation processes in liquids. Over limited ranges these usually conform quite well to Arrhenius expressions of the forms $\tau = A \exp (\Delta H/RT)$, ΔH usually being of order several kilocalories per mole. At low temperatures, however, more drastic changes have been observed in many substances, especially as glassy behavior is approached; at such temperatures, the measurements can often be represented empirically by an equation of the form $\tau = A \exp B/(T - T_\infty)$, where T_∞ is 10 to 20 degrees below the experimental glass temperature. Examples of dielectrics found to show this behavior are aliphatic alcohols and glycols [Davidson (89), Dannhauser & Cole(67)] and alkyl halides [Denney (90)]. Williams, Landel & Ferry (91) have found similar behavior in viscoelastic relaxation of polymer solutions; the Williams, Landel & Ferry equation proposed by them is of the same form as the dielectric equation and they further find that the coefficient B is proportional to T_∞.

The free-volume theories described predict temperature dependence quite similar to that observed at constant pressure. In the theory of Cohen & Turnbull this results because the available free volume at constant pressure increases linearly with temperatures in excess of a temperature T_∞, at which temperature this volume is zero. Some question as to the adequacy of the treatment is, however, raised by data of Gilchrist, Earley & Cole (92) for dielectric relaxation of 1-propanol and glycerol as a function of pressure. These data show that at constant volume the temperature dependence is still more rapid than exponential, whereas the theory predicts a variation only as $T^{1/2}$ under these conditions. Data of this kind for other systems and relaxation processes are meager or non-existent, but when available should give valuable evidence.

The dispersion observed in polar liquids and mixtures often shows a frequency dependence considerably different from that predicted by the Debye equations. The deviations are always in the sense that the dispersion and absorption are found over a wider range of frequencies, but they are of several kinds in other respects.

The simplest type of behavior can be represented by a superposition of a few discrete relaxation functions $a_i(1 + i\omega T_i)^{-1}$ with relaxation times T_i and relative amplitudes a_i; this superposition can give either an unresolved

broader absorption range or two or more distinct maxima in ϵ''. Data for protein solutions have been analyzed by Oncley (83) in this way, using Perrin's theory for rotation about the principal axes of an ellipsoid representing the molecule. Kirkwood & Shumaker (93) have shown, however, that very similar effects can arise from proton migrations among basic sites on the protein surface without permanent dipole orientation. O'Konski (94) has suggested that similar effects may result in ionic displacements in polyelectrolyte solutions and has analyzed the consequences in terms of equivalent surface conductivities.

Another source of more than one dispersion region for polar molecules can be polar groups in the molecule, if these have some relative freedom for separate orientations. Davies & Meakins (95) have found two distinct absorption regions in substituted phenols and other "flexible molecules"; the evidence clearly associates the faster process with reorientation of the hydroxyl group and the slower with dipole displacements requiring motion of bulkier parts of the molecule. Three dispersion regions have been found in aliphatic alcohols by Cole *et al.* (67, 96), Magat (97), and Reinisch (98); the interpretations have been in terms of relative motions of OH and CO groups in hydrogen-bonded chains, and of the terminal molecules in such transient chains [Brot (99, 100)]. A still different model, which can lead to several discrete processes, involves the consequences of non-equivalent sites and barriers to reorientations; these are discussed in the next section.

Two common, and in most cases still puzzling, types of relaxation are experimentally characterized by broad continuous-frequency ranges of dispersion, whether symmetrically on a logarithmic scale about the frequency of maximum absorption (circular arc locus of ϵ^*), or primarily at frequencies greater than that for maximum absorption (skewed arc locus of ϵ^*).

For dilute solutions of polymers with attached polar groups, Hammerle & Kirkwood's further development (101) of the Fuoss-Kirkwood theory predicts an approximately symmetrical broadening from a rotational diffusion analysis of coupled polar-segment motions in the polymer chain. A considerable amount of experimental work on such solutions has been done by de Brouckère (102, 103) and by Mikhailov (104, 105); the evidence is somewhat confusing and in some cases does not seem to show the predicted molecular weight dependence. The review article by de Brouckère & Mandel (106) should be a valuable guide; unfortunately the writer was not able to obtain a copy before submitting this review.

Broadened dispersion and loss regions in polymers are predicted by normal mode treatments of coupled motions [see Zimm (107)], and can be represented by a distribution function of relaxation times. Wada has given results of a series of measurements of polypeptides in solution (108). In a theoretical discussion (109), he has estimated the dipole moment of the α-helix, the dielectric constant from a cylindrical Onsager cavity model, and the effect of polydispersity in broadening the observed dielectric loss spectrum.

The details of the polymer model are not appropriate for other molecules showing broad relaxation spectra, but the cooperative nature of the treatment may find a counterpart in an analysis of coupled motions that incorporate physical pictures similar to those of Beuche and of Cohen and Turnbull. Much the same suggestions can be made about the skewed arc loci observed for a number of polar liquids, especially at low temperatures. Schrama (76) and Gross (110) have pointed out that relaxation functions such as $[(1+(i\omega T)^{1-\alpha}]^{-1}$ (circular arc) and $(1+i\omega T)^{-\beta}$ (skewed arc) can be generated by solutions of diffusion-type differential equations in which the distributed effect comes from interactions of adjacent elements in space, but the writer knows of no detailed theories incorporating such effects in convincing molecular terms.

The foregoing discussion has necessarily been confined to some examples of various types of behavior and to some of the theories so far proposed for their interpretation. The experimental evidence is still far from complete for many interesting liquids, especially those composed of small molecules and at wavelengths below 1 cm. An apparently quite general experimental result has emerged from extrapolation of microwave dispersion data to the limit of infinite frequency, namely, that the limiting value ϵ_∞ is significantly larger than n^2, the square of the refractive index at visible or near infrared frequencies, even after any reasonable allowance for atomic polarization. Poley (111, 112) found this discrepancy for substituted polar benzenes; similar results have been found by Heineken & Bruin (113) and by Rampolla, Miller & Smyth (114) from measurements at 3 mm. wavelength. In most cases, there is no evidence to indicate whether the difference results from resonance- or relaxation-absorption processes or both. Data at submillimeter wavelengths will be needed to settle such questions, and there is little doubt that such measurements, when feasible, will give interesting information.

DIELECTRIC BEHAVIOR OF SOLIDS

The body of recent information and theory for solid dielectrics is not reducible to any brief series of simple statements, even after excluding such topics as ferroelectrics, electreto, and solid polymers. Only a limited number of results, principally for substances containing polar molecules, can be singled out for mention here.

Although freezing a polar liquid frequently freezes out freedom of dipole orientation at the same time, a surprising number of systems have dielectric constants significantly larger than expected for induced polarization, especially in higher temperature "rotator" or "plastic crystal" phases stable at temperatures not too far below the melting point. Smyth (4) has tabulated dielectric, thermal, and structural data for more than 200 molecular solids; a 1953 review in this series by Zimm, Oriani & Hoffman (115) on coöperative aspects of phase transitions has some discussion of dielectric properties.

When considering molecular aspects of solids dielectric behavior, it is important to keep in mind other possible effects and complications peculiar

to solids. The first is that heterogeneities or mixed phases can give rise to interfacial polarizations, which can be so similar experimentally to dipole orientation effects that other evidence may be necessary to resolve the ambiguities. An extensive literature has developed on dielectric behavior of mixtures, suspensions, and electrode interfaces. Dryden & Meakins (71) have outlined some of the effects, and Hamon (116, 117) has reviewed low frequency loss behavior in solids which often arises from such causes. Voids in the body of experimental samples or at measuring electrodes give rise to interfacial effects and serious errors if the dielectric constants are large, and are certainly a major reason for conflicting data on such substances as ice and hydrogen halides. The nature of the effects and means of circumventing them have been discussed [Auty & Cole (118), and Brown & Cole (119)].

Two or three principal dielectric constants may be necessary to characterize crystals of less than cubic symmetry. In most cases, however, measurements have been made on mixed crystals, giving some sort of weighted average static dielectric constant; for relaxation there may well be a compounding of several molecular and interfacial effects. The important special case of ice is an exception, as Humbel, Jona & Scherrer (120) and Steinemann (121) have found a single Debye relaxation in single crystals regardless of field direction, with about 15 per cent anisotropy in static values. Data for polycrystalline ice show intermediate simple behavior.

The cooperative interaction of rigid or polarizable dipoles on lattice sites by dipole-dipole coupling is a classic problem in statistical theory, which has been treated in various degrees and kinds of approximation for dielectric constants and thermal equilibrium properties. Most of the assumed forms of potential energy of interaction lead to prediction of one or more solid-phase transitions as low temperature ordering sets in on cooling. Lax (122) and Toupin & Lax (123) have calculated equilibrium behavior for electrostatic coupling of permanent plus induced point dipoles on a simple cubic lattice in the spherical model, in which only the sum over molecules of permanent dipole moments is kept fixed rather than the true condition that all are individually fixed in magnitude. The model predicts a transition temperature close to the lower value of 89° in solid HBr (which, however, has face-centered structures); the experimental dielectric constant shows a sharp lambda-type maximum which is predicted by neither this nor Kirkwood's earlier theory (124).

Krieger & James (125) have given a critical discussion of pair interaction potential approximations, and have shown that a potential of form $A \cos \theta + B \cos^2 \theta$, where θ is the angle between molecular axes, can give one or two phase transitions for varying magnitudes of A and B. The dielectric and other evidence on molecular orientations and phase transitions in hydrogen halides, which show a variety of transition behavior and are often cited in such theoretical developments, has been discussed [Powles (126) and Havriliak & Cole (127)].

The role of lattice defects in permitting dipole orientations has often been considered in connection with a variety of problems. The unique prop-

erties of ice have recently been treated, principally in terms of Bjerrum's fault site model (128) in which the defects consist of vacant or doubly occupied proton sites between adjacent oxygen atoms. Gränicher (129) and Eigen & de Maeyer (130) have reviewed the variety of evidence; more recently Onsager & Dupuis (131) gave a symposium discussion which at this writing has not been published in detail.

A quite different problem of considerable interest is the polarization produced by paired impurity sites in ionic crystals [as first found by Breckenridge (132)] that can act as dipoles and produce significant loss effects by their rearrangement in the crystal structure. Dryden & Meakins (133) have made extensive studies of alkali halide crystals doped with divalent cation impurities and have had remarkable success in calculating the observed relaxation effects from a model of ion jumps into a vacancy adjacent to an impurity ion; the barrier energy for the easiest route between interfering neighbors was calculated in terms of elastic-strain energy estimated from measured compressibilities.

The simple model of dipole polarization in solids, by redistribution of populations between two possible low-energy dipole orientations in space, has been discussed by almost every writer on the subject from Debye on. If more than two such sites exist with non-equivalent energy minima and intervening barriers, multiple relaxation times are predicted by activation-rate theory treatments of transitions induced by an applied field. Meakins (134), Dryden (135), and their co-workers have proposed this kind of explanation for observed reorientation effects of long-chain esters, bromides, and ketones.

Hoffman (136, 137) and Axilrod (138) have discussed in detail the theoretical possibilities for single axis rotators having three to six potential minima on rotation about the axis. The maximum number of possible relaxation times from a normal mode treatment of the coupled-rate equations for site occupations is one less than the number of sites; usually the predicted possible loss regions coalesce at higher temperatures and have appreciable amplitudes only if the energy differences between sites are not too great.

A particularly favorable system for studying such possible effects involves dipole molecules occluded in the cagelike vacancies of quinol compounds or the tubular cavities of solid urea, because dipole-dipole interactions can be expected to be weak. Lauritzen (139) has made a remarkably successful prediction of the multiple loss regions found by Meakins for ketones and bromides occluded in urea. The energies of sites and barriers of the sixfold potential for rotation of the polar group in the surrounding honeycomb of urea molecules were calculated with Lennard-Jones and volume overlap energies.

A number of investigations have been reported for crystalline alcohols and a variety of organic and inorganic hydrates. Meakins & Sack (140) have suggested the importance of hydrogen-bonded chains for appreciable absorption; in long-chain primary alcohols, considerable direct current

conductivity is found and may be attributable to proton transfer in hydrogen-bonded chains. Dryden & Meakins (71) have given an excellent critical review with references.

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COLLOID CHEMISTRY[1]

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MEETINGS AND BOOKS

This review will include a somewhat critical survey by the author of se-
lected topics in colloid and surface chemistry that are in current fashion, but
will exclude reference to work on the solid/gas interface, catalysis, and
polymers. The period covered is that between the second and third interna-
tional meetings on Surface Chemistry held in London, April 1957, and
Cologne, September 1960. The London meeting was reviewed from the pre-
prints by Professor Zettlemoyer in the 1958 *Annual Review of Physical
Chemistry.* Also, besides the two National Colloid Symposia published each
October in *Journal of Physical Chemistry,* several symposia were held at the
American Chemical Society, Colloid Section, biannual meetings on selected
topics in Colloid Chemistry. These included "Micelles in Non Aqueous
Media" (1), "Energetics of Surfaces and Interfaces" (2), "Wetting Proc-
esses" in honor of F. E. Bartell (3), "Biological Function and Structure"
(3), and "Solid/Liquid Interface" (4) (not all these papers appear published
in full). A very useful review on "Immersional Heats and the Nature of the
Solid Surface" by Chessick & Zettlemoyer appeared in *Advances in Catalysis*
(5). This will be referred to later in work on contact angle and surface
energies, which require a more concise approach to their understanding.
Zettlemoyer published a more general review relating to techniques in surface
chemistry (5a).

The Faraday Society, Colloid and Biophysics Section, held a symposium
on "Configurations and Interactions of Macromolecules and Liquid Crys-
tals" in 1958 (6). A high proportion of the papers that were presented came
under the heading of polymers or polypeptides and nucleotides, but the
theoretical papers and those on soaps and soap amphiphile associations were
very pertinent to fundamental colloid chemistry.

Kitchener and colleagues have produced two very useful reviews. Their
"Current Concepts in the Theory of Foaming" (7) collected and brought up
to date, in a constructive manner, all experimental and theoretical ap-
proaches in a field that had previously been most empirical. Their second re-
view was of an informal meeting held under the auspices of the Colloid and
Biophysics Section of the Faraday Society (8) on the "Electrical Double
Layer in Colloid Science." Ideas discussed at this meeting will be referred
to later in this article.

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Surface Phenomena in Chemistry and Biology (9), edited by Danielli, Pankhurst & Riddiford, brought out by friends and former research students of N. K. Adam to honor him on the occasion of his retirement, includes 23 contributions by surface chemists, mainly critical review articles with some original papers, and the references are especially useful.

A book of special interest for bio-colloid chemists deals with the chemistry, structure, and permeability of the nerve membrane [Nachmansohn (10)]. This topic presents challenging problems to physical chemists who are working on models for such biological systems as the structure of lipo-protein leaflets at cell surfaces, their selective permeability to sodium and potassium ions, and the chemical activity of enzymes at these interfaces.

EQUATIONS OF STATE FOR MONOLAYERS

Application of the equations of state of monolayers derived from the air/water and oil/water interfaces to such practical problems as the control of chemical reactions at interfaces by surface pH or surface charge or the formation and stability of micro emulsions has been of interest to several research workers in these fields of investigation.

Ever since Derjaguin (11, 12), and Verwey & Overbeek (13) derived an equation of state for the free energy of formation of the electrical double layer at an interface from the Gouy theory, efforts have been made to bring this free energy term $\Delta\pi = \int_o^{\psi_o} \sigma d\psi$ (σ is surface charge per cm.^{2}, ψ is the Gouy double layer potential) into the equation of state for partially ionized monolayers and prove experimentally the various equations for non-ionized monolayers, partially ionized monolayers, and fully ionized monolayers.

$$(\pi + \beta N - \Delta\pi)(A - A_o) = kT$$

[βN is the Guastalla (14, 15) term for the cohesion forces between the hydrocarbon portions of the film forming molecules, A_o is the co-area, $\Delta\pi$ is the electrical term]. Matijevic & Pethica (16, 17) applied the above equation of state to the non-ionized form (leaving out $-\Delta\pi$) by measuring the surface tension-concentration curves at different temperatures for octanoic acid at pH 2 in its associated form and obtained very good agreement between the experimental and theoretical curves, thus establishing the Guastalla-Davies (15) nonpolar cohesional term. This cohesional term is removed, of course, when the surface tension curves are measured at the oil/water interface (15). Matijevic and Pethica, by now measuring the surface tension concentration curves at pH 12 for sodium octanoate could bring the ionized surface electrical term $-\Delta\pi$ into the equation of state and compare the theoretical term as derived by Davies, Verwey, and Overbeek, for the energy of formation of the electrical double layer. The π-A theoretical curves deviate drastically from the experimental curves at areas less than $100A^2$, and give quite good agreement at areas greater than $200A^2$. Similarly, by comparing the theoretical heats of formation of the double layer calculated from the theory of ionized surfaces (13) with the experimental equilibrium integral heats of adsorption,

one obtains good agreement at high areas per molecule, but poor agreement at small areas. The actual sign of the heats of adsorption, experimental to theoretical, change from positive to negative at areas below $75A^2$. This disagreement of theory with experimental results again shows itself at high surface concentrations with the electrical measurements of the double layer as measured by surface potentials and electrophoresis, and will be discussed later.

The influence of salt concentration on the free energy of formation of the electrical double layer as shown in the $-\Delta\pi$ term by application of the same theories, and tested out experimentally in the π-A curves and heats of micelle formation for long chain sulphates by Matjevic & Pethica (18, 19, 20) and long chain phosphoric acids by Payens (21), shows strong diminution of surface pressures at high salt concentrations for the completely ionized monolayers. This effect can be explained by consideration of the position of the counter ion. At high concentration it will penetrate between the negatively charged molecules in the interface, and at low concentrations it will leave the monolayer and form a diffuse layer in the underlying solution.

This concept has been considered in detail by Davies (22, 23) in deriving an equation of state for fully ionized monolayers at the oil/water interface $\pi(A - A_o) = 3kT$, where the double layer potential ψ_o must be greater than 100 mv. and at high areas A_o can be neglected (24); for non-ionized monolayers $\pi(A - A_o) = kT$.

A good review of the application of the energy of the formation of the electrical double layer, as conceived by Gouy as a term in the equation of state for (ionized or partially ionized) monolayers, has been given by Payens (25). This includes the theoretical work up to 1956. The attempts to prove the theory by experiments is more recent and is described in this review.

Sparnaay (125) has given a theoretical treatment for the interaction between two cylinder shaped colloid particles, which is a compromise between the interaction between two spheres or two plates, as previously investigated.

SURFACE POTENTIALS

Surface potential is the work necessary to move a unit charge through an interface, whether this interface is at air/water, oil/water, solid/gas, or solid/water, and is usually used as a differential potential obtained by following changes at the interface such as adsorption phenomena or chemical reactions taking place at these interfaces. The surface potential difference measured at a clean gold surface and a clean platinum surface gives, e.g., the contact potential between gold and platinum. This contact potential can be used as a convenient reference potential for absolute values when following adsorption or other phenomena taking place at solid surfaces, and is actively being used by the author (26) for this purpose.

The measurement of the surface potential can be carried out conveniently in two ways. One involves ionizing a 2 to 3 mm. low dielectric gap (gas or liquid) with a suitable radioactive source giving a conductivity of approxi-

mately 5.10^{10} ohms between a small metal electrode and the surface of the aqueous solution or conducting solid (26). The internal resistance of the electrometer measuring device must be considerably greater than the above quoted resistance. The second method uses the Kelvin principle: measuring the deflection on an electrometer by moving a small plate above the surface, or by bringing the deflection back to zero by superimposing an opposite potential on the plate. The disadvantage of the ionizing gap method is that it cannot be used without a gas in the circuit, but it is directional and has a small solid angle and consequently can pick up localized potential changes. The moving-plate technique can be used in gas-free systems, but must measure mean potential changes over comparatively large areas of interface. Comparative measurements using the two techniques have been carried out by Davies (27) for oil/water interfacial adsorption problems and by the author for solid surfaces. Fowkes (28) has studied solid surfaces with a vibrating plate technique (an extension of the Kelvin method) using a cathode amplifier. The vibrating plate technique was originated and extensively used by Zisman for adsorption phenomena at the air/water interface.

The surface potential difference on depositing a monolayer at an oil/water or air/water interface is given by the expression (27)

$$\Delta V = \frac{4\pi n\mu}{D} + \psi_o + \psi_{oil} = 0$$

where μ is the vertical component of the resultant dipole of the film forming polar group in an interfacial medium of dielectric D, n is the number of molecules per cm.^{2} in the monolayer, and ψ_o is the potential of the diffuse double layer in the aqueous phase and is the total zeta (ζ) potential. This potential will change 58 mv. for every tenfold change in concentration of a uni-univalent salt and is directly equivalent to the Gouy ψ_0 and in simplified form is

$$2\,\frac{kT}{e}\sinh^{-1}\frac{(134 \times 10^{-16} \times n)}{\sqrt{C}}$$

This has been shown experimentally to be valid (27). ψ_{oil} is the diffuse ionic double layer potential which can be built up in an oil phase, where ions have a certain solubility. This diffuse ionic double layer cannot form in paraffins or air for example, hence the surface potential ΔV has a finite and constant value for these systems. But with somewhat polar oils such as benzene or bromobenzene or octylalcohol, the surface potential ΔV will fall rapidly with time to zero according to the capacity and resistance of the system and as the ions dissolve into the oil phase from the aqueous phase and build up an opposing ψ_{oil} potential in the oil phase as predicted by Dean, Gatty & Rideal (29). The three potentials mentioned in the ΔV equation have very important implications in several fields of investigation. For example, Haydon (8) has determined ψ_0 in the aqueous phase, both by interfacial tension measurements at an oil/water interface applying the Gibbs and the Gouy equations

(27) for alkyl sulphate and alkyl substituted amine salts adsorptions and by surface potential measurements. He has shown that the ζ potential as measured by micro-electrophoresis of emulsions droplets of the same system is only a small part of the real double layer potential ψ_o. Haydon explains this by suggesting that only a fraction of the diffuse double layer is sheared off by the electrophoresis, the plane of shear depending on the charge density and the nature of the water involved with the dipoles of the film forming molecules. This bound water of course is responsible for the dielectric constant of the interfacial film, which plays an important part in the surface potential term for the fixed dipoles.

That ψ_{oil} might play a similarly important part in the charge at oil/water interfaces has never been emphasized in the literature. This may be why water droplets in oil in micro-emulsions are stable and are almost certainly charged, and this effect may also account for the properties of powders or solids stabilized and dispersed by surface active agents in nonaqueous media (30, 31) which can migrate in an electrical field.

Recently Albers & Overbeek (32) have shown that macro-emulsions of water drops in benzene stabilized by metal soaps have a surface charge as measured by their electrophoresis. This is very reasonable since Davies (27) has shown that a diffuse ionic double layer can exist at the benzene/water interface, both in the water and benzene phases, and the surface potential falls with time in the presence of a monolayer of a surface active agent. It would be very interesting to see if a surface charge can be obtained with water droplets stabilized in paraffin where no diffuse double layer can exist as shown by the constant ΔV value at the paraffin/water interface (27). The original water-in-oil emulsions, as discussed by Albers & Overbeek (32) and made by Schulman and Cockbain, were water droplets in paraffin (Nujol) and should consequently have no surface charge. The problem of stable micro- or macro-emulsions of water droplets in paraffin stabilized by nonionic agents will have to be considered; perhaps a hydrated surface can exist orientated in the nonaqueous continuous medium. Koelmans & Overbeek (31) considered that non-ionics did not stabilize solids in nonaqueous media, owing to the impossibility of producing a surface charge with these compounds. The electrophoresis of the micro-emulsions owing to their small droplet size will have to take place in a Tiselius diffusion cell and can be measured by a schlieren technique similar to that used for measuring their sedimentation in an ultracentrifuge. Emulsions will be discussed later in the review. The use of surface potentials involving the $4\pi n\mu$ term in the ΔV equation has been given by Fort & Alexander (33) in their study of monolayers of the alkyl vinyl compounds and their polymers. Influence of the neighboring polar groups on the vinyl double bond is especially interesting; likewise, the influence of weak acid solutions on the vinyl alkyl ethers but not on the vinyl stearates has interesting implications for a fundamental study of polymerisation kinetics by monolayer techniques.

CHEMICAL REACTIONS AT INTERFACES

The influence of the surface potentials (the measurement of which in-
cludes the surface charge, ionic double layer, and dipolar structure of the
molecules at the interface) on the course of chemical reactions taking place
at an interface has recently been shown for the rates of hydrolysis of certain
esters [Davies (34, 35), Davies & Llopis (36), and Dawson & Bangham (37,
38, 39)]. The first authors show how the control of the surface pH by addi-
tion of positively or negatively charged surface active agents intermixed
with an ester monolayer, can, in acid solutions where the ester hydrolysis is
catalysed by H^+ ions, greatly inhibit or accelerate respectively the rate of the
reaction. In the first case, owing to the positive surface charge, the surface
concentration of hydrogen ions ($C^s_{H^+}$) is less than the bulk ($C^b_{H^+}$), and in
the second case, owing to the negative surface charge, it is greater. The addi-
tion of alkyl sulphate molecules to a cholesterol formate monolayer ($C^s_{H^+}$
$> C^b_{H^+}$) produces a thirteenfold increase in the velocity of hydrolysis in acid
solution, and the addition of an alkyl substituted amine produces a cor-
responding decrease. The theoretical equation involving the double layer
potential can be proved experimentally (34, 35). The second series of authors
use the addition of similarly charged additives to lecithin (phosphatidyl
ethanol cholin) films. This controls the hydrolysis of the glycerol ethanol
cholin linkage to the glyceride position of the molecule by an enzyme at its
pH of optimum activity (lecithinase or phospholipase). In this case, the sur-
face charge of the monolayer controls the rate of hydrolysis of the ester
group by quite a different mechanism from that in the previously quoted
example. Bangham & Dawson (37, 38) show that emulsions of lecithin do not
hydrolyse with the phospholipase enzyme unless the emulsion is given a nega-
tive charge by the addition of an alkyl phosphate. Such activation is removed
by addition of neutralizing ions, e.g., uranyl, calcium, or thorium, or by add-
ing surface active agents of opposite charge such as alkyl substituted amines.
It was further shown by monolayer techniques (39) that the enzyme can
hydrolyse low pressure surface monolayers of lecithin ($<$30 dynes/cm.) and
that the rate of hydrolysis is accelerated by increasing the surface concentra-
tion of the lecithin molecules by raising the surface pressure, *without* any
negative surface charging. On highly compressed monolayers of lecithin
where the surface concentration is equivalent to that of a micelle or emulsion
droplet at surface pressures $>$30 dynes/cm., the hydrolysis ceases. The hy-
drolysis can be immediately reactivated by the addition of a negatively
charged amphiphile, as in the case of the bulk hydrolysis for the lecithin
suspensions. This activation can again be inhibited by removal of the sur-
face charge. It has been shown by Fraser, Kaplan & Schulman (40) that leci-
thin films can prevent the surface denaturation of proteins at oil/water inter-
faces since protein molecules do not penetrate the uncharged lecithin mono-
layers. Surface charged lipid monolayers are penetrated by protein molecules
with a charge opposite to that of the surface, according to the isoelectric

point of the protein in solution, and are progressively denatured, sometimes reversibly (40, 41). The presence of the negative amphiphile molecules in the condensed uncharged lecithin monolayer sensitizes this monolayer to penetration and hence hydrolysis by the protein molecule or enzyme. At low surface pressures the enzyme molecules can penetrate the lecithin film on their own free energy and hydrolyse the ester group. It is interesting that this is the reverse of the action of the lecithinase in Cobra snake venom (42) where inhibition of the hydrolysis, in this case of the unsaturated fatty acid radical from the lecithin molecule, takes place when the surface pressure of the lecithin film is increased. The removal of the double bond from the interface inhibits the reaction, as in oxidation reactions, in which orientation of the molecules rather than the surface charge controls the kinetics of the reaction. The implication of the above quoted examples in relation to the understanding of such important biocolloidal problems as blood clotting, complement fixation, and Kahn adsorption phenomena is very apparent. Payens (43, 44) has applied similar ideas to enzyme reactions and lipoprotein associations that take place on the surface of milk fat droplets where the surface pressures of the protein molecules, in relation to the surface pressure of fat monolayers, play an important part.

COLLOID STRUCTURES

Binary Systems

The combination of monolayer techniques with the high resolution electron microscope and low angle x-ray equipment is starting to play an important part in elucidating the detailed structure of both natural and synthetic colloid systems. The interpretation of the structure of the synthetic systems has also been greatly helped by the application of biological staining techniques. The study of the synthetic systems has been greatly stimulated by the work of the biologists who showed that the nerve membrane has a lamellar bimolecular leaflet structure of lipoprotein 70A in thickness (45, 46), as seen with an electron microscope after osmic acid or permanganate staining. Such structures are also seen as the external membrane of an amoebe proteus (47), red cells, and many other biological systems such as the kidney tubule.

Another important aspect of the bimolecular leaflet membranes on cell surfaces, to the physical chemist, is that they possess highly selective permeability properties to potassium and sodium ions and to simple organic compounds. This has stimulated investigation of physical chemical model systems to explain the selective permeability properties (48).

Stoeckenius (49), by staining the hydrocarbon portion of potassium linolenate in the neat soap region with osmic tetroxide, whereby the nonconjugated double bonds are intermolecularly interlinked in the upper portion of the hydrocarbon chain, obtained a striated structure of 41A spacing as seen in the electron microscope at magnifications of 80,000 to 160,000.

This dimension is identical to that obtained by Luzzati and associates, (50), using x-rays, where the repeat unit is now obtained from scattering due to the carboxyl polar groups as compared to the hydrocarbon scattering with the osmic acid staining in the electron microscope. The soap sample is microtomed in a polymer ester methacrylate substrate, as if it were a biological specimen, for viewing in the electron microscope (49). A cephalin myelinic gave a similar repeat spacing of 41A in the electron microscope, which is too small to fit the entire molecule and the water. In this aspect the x-ray work of Luzzati *et al.* (50, 51) is of considerable importance since he shows that on dilution of a soap from the "neat" phase (75 per cent) to the "middle" phase (40 per cent) at 100° C. a new structure appears in which the soap molecules are orientated radially in cylinder structures in an equidistant nematic state. The polar carboxyl groups are in a crystal or solid array structure whereas the hydrocarbon chains attached to them are in a liquid array. This explains diameters for the cylinder and layer structures that are too small for the double layer, fully stretched molecules as occur in the crystal state. Further, this work (50) has shown that other new structures exist in the intermediary soap water phases, in which the uniform cylinders of soap molecules arrayed in a bimolecular leaflet occlude water in the center, the whole structure existing in a hexagonal pattern. A structure of exceptional interest for workers investigating micelles in soap solutions is that of the rectangular boxes of soap molecules as now established by x-ray techniques (51); confirmation of these structures as seen in the electron microscope by staining would produce a considerable advance in our knowledge of colloid systems in general. Peri, using calcium salts of detergents, obtained electron microscope pictures of swollen detergent micelles in oils (124).

Stoeckenius, by diluting (49) cephalin myelinics in water and adding a protein under conditions in which the protein molecules would penetrate a monolayer of cephalin, obtained a lipoprotein leaflet structure 70A thick as seen in the electron microscope after staining with osmic acid. This leaflet synthetic structure was indistinguishable from the natural membrane structures seen at cell surfaces.

Dervichian (113) has produced an interesting paper on mixed crystals of fatty acids with different hydrocarbon chain lengths ($C_n + C_{n+4}$ or $C_n + C_{n+6}$) showing direct stoichiometric associations in bulk phases.

Heckmann (52, 53, 54) originated an interesting new technique for investigating the anistropy of colloidal systems. He measured the ratio of the electrical conductivity of the system both in direction of flow and at right angles under a velocity gradient of a colloidal solution in a couette between two concentric cylinders with the frequency of rotation and the temperature being varied and controlled. The size and shape of the micelles and structures measured by this technique give good confirmation to Luzzati's results for rod or cylinder shape aggregates and to those of rod micelles in concentrated detergent solutions. Although it is possibly outside the scope of

the review, Robinson *et al.* (55, 56) have shown some interesting types of liquid crystals in the nematic state that spiral clockwise or anticlockwise according to the type of optical isomer *laevo* or *dextro* of some simple polypeptides that are strongly intramolecularly hydrogen bonded and in helical structure. This type of twisted liquid crystal has hitherto been observed with the cholesterol esters. The theory for the structure of the various liquid crystal states has been criticized and enlarged by Frank (57), especially in relation to the cholesteric states.

TERNARY SYSTEMS

The creation of liquid crystals and liquid crystalline phases by the addition of amphiphile molecules such as alkyl alcohols, sterols, alkyl amines, and fatty acids to soap or detergent water phases has been extensively examined by Lawrence *et al.* (58, 59, 60) and Dervichian (61). They have produced ternary phase diagrams showing the effects of the different amphiphile compounds on increasing the solubility of the soaps and detergents and different types of liquid crystal or myelinic structures formed. The penetration phenomena of the soap or detergent molecules into the alcohol or cholesterol structure, similar to the penetration of these molecules into monolayers of the alcohols at the air/water interface, has been discussed in relation both to the change in solubility of the system with water and also in the mechanism of detergency (62). The cryoscopic forces discussed by Lawrence do not take into account the very high spreading pressures at interfaces exerted by the mixed films of these associations.

These spreading pressures can well be greater than the interfacial tensions found at any separation of the liquid crystal into two phases. This might well give rise to negative interfacial tensions that would be immediately responsible for the interface breaking up into small-diameter large interfacial area structures such as myelinic or micro emulsions; this is important for the quaternary systems.

QUATERNARY SYSTEMS

A subtle combination between the hydrocarbon of the oil phase and the complex between the amphiphile and the soap or detergent molecules at the interface between the oil and water has been found [Schulman, Stoeckenius & Prince (63)] to be essential before micro-emulsions (transparent oil and water dispersions)are formed. The triple complex (amphiphile-soap-hydrocarbon) at the interface is almost certainly responsible for liquefying the interfacial mixed film and for producing a negative interfacial tension. This enables very small droplets and maximum interfacial area to be the stable equilibrium system. The phase inversion can be controlled by the charge or hydration of the interfacial mixed film. By controlling the concentration of the amphiphile and soap molecules, in the presence of the appropriate oil phase, droplets of either oil-in-water or water-in-oil could be made ranging

in size from those of swollen micelle 75A diameter to droplets around 1000A diameter. For each individual concentration the droplets were uniform, especially when very small. The oil droplets can be readily stained with osmic acid and seen directly in the electron microscope, substantiating the theories for the structure of the isotropic transparent oil/water systems. The stained oil droplets below 350A in diameter are not visible in the high resolution electron microscope unless the contrast is enhanced by the use of an inverted negative, i.e., by background staining with phosphotungstic acid, which enables oil droplets of 75A diameter to be visible in the electron microscope (64).

Palit (65) has studied these types of systems using associations between quaternary ammonium soaps and chlorinated hydrocarbons such as chloroform and chlorbenzene that form liquid crystals with water, and micro-emulsions with nonpolar solvents.

Monolayers and Mixed Monolayers

A good critical review article by Dervichian (66) discusses those associations formed in mixed monolayers and by penetration and ejection techniques, whereby the significance of plotting the rate of ejection of one species of molecules from a mixed monolayer at constant pressure is emphasized to establish the existence of stoichiometric complexes.

Ries (67) has continued his work on electron micrograph pictures of monolayers; of especial interest are his uniform, high pressure, stable, mixed films produced with stearic acid and polyvinylacetate (68). Considerable interest is also now being shown in mixed monolayers of stearic acid or stearyl alcohol with hydrocarbons (69, 70) and with benzene (71), which show remarkable stability. The significance of these associations has been emphasized in the process for forming micro-emulsions and also in films being investigated for water evaporation retardation (70), where entrapment of the solvent in the monolayer causes trouble.

Sobotka (72) has shown that certain films at collapse pressure build polymolecular layers, e.g., triiodostearic acid, which forms a trimolecular layer; this reopens the old controversy of the structure of collapsing long chain soap films, originally postulated by Lyons and Rideal. Sobotka (73) also considers the structure of multilayers of stearic acid in the absence and presence of polyvalent cations.

In this context it is useful to mention the work of Joly (78) on the rheological properties of monolayers under shear. By transplanting energy to the molecules, dynamic phase changes can be induced, especially in the higher order phase transformations of Ehrenfest in the solid states. This work, together with visco-flow of monolayers, has been reviewed (78) and has application to the flowing of cetyl alcohol films on water for evaporation retardation purposes.

Boyd has two papers on the energy relations for single component mono-

layer systems (102, 103) and mixed monolayers. In the first he considers that the entropy of the molecules in a monolayer warrants only rotation of the molecules ard not translational freedom of movement. This has implications in our understanding of the higher order transformation points of Ehrenfest and interpretation of possible two-dimensional phase transition points.

The liquid crystal states for soaps [Luzzati (50, 51)] opens to doubt the interpretation of the structure of condensed monolayers as hitherto envisaged. The polar groups can be in solid state structure with the hydrocarbon chains in a liquid state. This implies alternative structures, for the condensed states, to the packing of straight zigzag hydrocarbon chains as indicated by x-ray work for crystals.

Boyd's second paper deals with the surface viscosity measurements of fatty acid and fatty acid and alkyl alcohol mixed monolayers, with the former behaving as solutions. Complex interactions occur in the mixed monolayer as measured by surface viscosity changes at increasing surface pressure. This is important in foam stability problems, where an amphiphile molecule is added to the detergent to bring about surface viscosity changes and impede drainage.

CONTROL OF WATER EVAPORATION

A series of papers, mainly by Mansfield and colleagues, on the practical application of cetyl alcohol monolayers to water evaporation retardation problems have appeared in Australian journals. This continues his previous work on the subject and deals with such problems as estimating seepage in storage tanks in order to assess evaporation quantitatively (74). Effects of dust, wind (75), waves, and the rate of spreading (76) of cetyl monolayers are also considered in detail. Two notes by Mysels (77) on convection and heat transport in the water interfaces are considered in relation to the resistance and driving forces involved for evaporation. LaMer (104) has considered the effect of impurities on the cetyl alcohol monolayer to which the evaporation retardation is sensitive.

CONTACT ANGLE AND SURFACE ENERGY OF SOLIDS

Attacks on the rigorous validity of Young's equation (112) (for contact angles on solid surfaces) nearly always produce papers in support of the original equation. The equation has been derived mathematically by Johnson (79) on surface tension considerations in contrast to surface energies. He shows that gravity or adsorption do not enter into the equation if it is derived in this manner.

Cooke (80) has derived the equation using surface energies instead of surface tension and comes to the same conclusion. Bikerman (79a) insists that perturbation effects due to adsorption on the solid change the contact angle owing to strains in the solid and gives experimental justification. Yates (81)

shows that the solid also perturbs the adsorbed molecules as well as the surface of the solid, so it must be expected that the controversy will continue.

Schulman & Leja (82) have inverted the usual technique of spreading liquids on solids by measuring the change of contact angle with time and the time of release of a captive bubble as the liquid displaces an air bubble from the solid surface; they use concentrations below the critical micelle concentration of the agent in the aqueous solution.

This has application to flotation systems for depressing the flotation of hydrophobic or natural floating gangues such as graphite, talc, etc. The time (and surface tension) of desorption of the air bubble is related to the chemistry of the additive (frother) in the aqueous solution and the adsorbed molecules on the solid surface and their associations at the various interfaces.

Carr (83) has shown by a bubble-pick-up technique of particles that the adhesion of the bubble is related to ageing effects at the air/water interface. This raises a discussion as to whether a double layer builds up at the solid surface (92), or at the air/water surface (bubble armoring); or whether a condensed film at the air/water surface prevents interpenetration of the molecules on the solid surface with the air/water interface film forming monolayers. It is evident from this experimental work on contact angle measurements with different liquids or solutions on different solids, that the surface energies of all three surfaces can be influenced. The contact angle change could be represented by plotting the difference of the surface tensions solid/gas and solid/liquid versus the concentration of surface active agent, keeping in mind that all interfacial energy terms are interdependent.

It would be very useful to have measurements of the surface energies or free energies of different solids and also of the heats of wetting of solids by liquids, with only small variations in the chemistry.

Certain attempts are being made in this direction. The surface energy of silicates has been ascertained [Brunauer (84)] by measuring the heats of solution in nitric acid and hydrofluoric acid of powders of the silicates and their components with different surface areas. The area determinations were made with water molecules by the B.E.T. (Brunauer-Emmett-Teller) method instead of nitrogen gas, which gave wrong results. Girifalco (85) has obtained results for the surface energy of different solids by measuring the surface energy of the liquid and the heat of immersion of the solid in the liquid. The heats of immersion of a large number of solids in different liquids are well reviewed and tabulated by Chessick & Zettlemoyer (5). They emphasize the implications of this information in many applied scientific fields.

The influence of the surface energy of the solid, as changed by adsorption of surface active agents or gases, is very important for the bulk property of solids, e.g., ductility, brittleness, or creep. Surface energy of solids has been reviewed by Kuznetsov (86) and the effect of surface active media on the deformation of metals by Rehbinder (87). It was shown experimentally by the Rehbinder school that if the grain diameter is greater than 4 per cent

of the specimen diameter, rates of creep are greatly increased as compared to the initial creep rate when surface active agents are present; up to thirty-fold rate increases are observed for copper wires [Amfiteatrova & Yampol'skii (91)]. These results could not be reproduced by Weiner (88, 89, 90) whose results with surface active agents have been confirmed by Nanis and Schulman.

While the Russian school considered that the surface active agents lowered the surface tension of the metal, Weiner and Gensamer considered that a blanket (with optimum thickness of 500A) of oxide or deposited metal such as copper on zinc acted as a barrier to the escape of dislocations thus increasing the brittleness of the metal. No effects were obtained on polycrystalline metals. If the tensile axis is orientated nearly perpendicular $(\chi = 83°)$ to the basal axis of the zinc single crystal, a 48 per cent decrease in fracture stress is observed; if the tensile axis is nearly parallel $(\chi = 3°)$, a 43 per cent increase in fracture stress is obtained in the presence of a zinc oxide, gold, copper, or zinc coating about 500A in thickness. In contrast to the Russian work, no effects were obtained with surface active agents, or with the coatings on polycrystalline metals. Quite different considerations have to be made for fatigue fracture (114 to 123).

ADSORPTION PHENOMENA AT LIQUID SURFACES

The kinetics of adsorption of organic compounds have been examined independently by workers in four different countries using four different methods on the same systems and their conclusions are far from unanimous. Sutherland (93), using a vertical hanging plate, showed that traces of metal ions in the underlying solution have great influence on the surface tension-time curves of sodium hexadecyl sulphate solutions, the time effects being related to the diffusion of the ions to the surface.

Hansen (94), using a vibrating jet method, and Garner (95), using a contracting jet method, investigated the adsorption to fresh surfaces over very small time periods of fractions of a second. They both concluded that the diffusion of molecules such as short chain fatty acids and alkyl alcohols to the surface is not the controlling factor, but an activation energy barrier that is not due to electrostatic forces of the polar group exists in the monolayer. Hansen considers a dimeric transition state located in the monolayer to be the governing factor; Garner believes that a monolayer penetration mechanism related to the hydrocarbon portion of the molecules and thus dependent on the chain length of the molecules fills that role. Defay & Hommelen (105 to 108) use, besides the vibrating or oscillating jet, a falling meniscus method and compare the static and dynamic surface tension methods. The water evaporation is a problem not hitherto considered with the static methods (108). It is interesting that these authors consider that diffusion plays the important role in the kinetics of adsorption of the same type of molecules investigated by the previous worker, and further believe that an activation

energy barrier to the adsorption only sets in for aged surfaces. The adsorption of dual component systems to the air-water interface has been studied by different methods. Research carried out by different laboratories to investigate the fundamental properties of foams has thus been extended. Alkyl alcohols and other non-ionic amphiphile water insoluble molecules can be brought into molecular dispersion in water by ionic detergent solutions. A mixed film forms at the air/water interface and mixed micelles are produced. Ross (96) has shown that the additive markedly changes the surface viscosity. Phase transitions that are temperature and surface tension dependent appear. Molecular associations are responsible for the formation of the condensed monolayers that expand and change into fluid monolayers at the phase transition temperatures. The condensed phases are responsible for low drainage rates in foams formed by these systems. The drainage of the solution from a frame holding a bimolecular leaflet, or leaflets, produces beautiful birefringent color changes until the black zone denoting the bimolecular soap lamellae appears. This phenomenon, extensively studied in recent years by Epstein *et al.* (97, 98), has recently been used by Mysels (99, 99a) to study the diffusion of the detergent in the solution between the leaflet, by time changes and movements of the interference color bands. Shinoda (100) and Fowkes (101) studied the composition of mixed monolayers in the presence of a series of different detergents with different amphiphile additives for purposes of foam stability of the mixed systems. The presence of the additive in the monolayer is shown to be responsible for the foam stability, in agreement with the work of Ross & Epstein, by increasing the surface viscosity and drainage time with susceptibility to phase transition temperatures. The association between pairs of detergent and amphiphile molecules also influences the packing of the mixed micelles and thus the C.M.C., critical micelle concentration, of the detergent.

The structure of dilute solutions of surfactants has been examined by a series of methods that produced some new concepts for the structure of colloidal systems.

Mukerjee *et al.* (109) have produced four papers showing that there is experimental evidence for the formation of dimers of ionic amphiphatic molecules in concentrations below the micelle point. The dimer has an opposite opposed double charge per unit and forms by association between the hydrocarbon chains and the dimerisation is in reversible equilibrium. The dilute detergent salt solutions give anomalous equivalent conductivities, and the transference numbers for the anion and cation in high dilution agree with the theory of dimerisation. By making large counter ions of hydrophobic nature, ion pairs are formed which compete with the formation of dimers.

With relation to the above interesting experimental work, the paper of Nash (110) entitled "Thermodynamic Barrier to Micelle Formation and Breakdown" is also of great interest. By diluting an ionic amphiphatic solution from concentrations above the C.M.C. to below, a nonequilibrium sys-

tem of micelles was shown to exist below the C.M.C. The period of time in which the existence of micelles below the C.M.C. was found to exist could be enhanced by the presence of dilute salt solutions from 30 to 70 hr. The methods used to establish the presence of micelles involved a fluorescing technique and the production of a sensitive viscoelastic system caused by the addition of β-naphthol. The visco-elastic system could be determined by its foaming properties. Further work is promised, using less drastic methods, to establish the existence of non-equilibrium micelle detergent solutions.

Micelle solutions of sodium elaidate and oleate have been examined by Tamamushi, Shirai & Tamaki (111) in relation to their hydrolysis. The hydrolysed fatty acid forms submicelles, which influence the C.M.C. of the true micelles. The elaidate has greater micelle forming power and solubilization for benzene than the oleate, which can be expected from the packing of the hydrocarbon chains.

Considerable research work has been carried out in the fields of adsorption of surface active agents onto solid surfaces, especially in the field of the electrical capacities of the resultant double layer at metal and mercury surfaces, and stability of solid particle dispersions and aerosols; this has been omitted from this review.

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SOME ASPECTS OF THE STATISTICAL THEORY OF TRANSPORT

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CHAPTER OUTLINE

I. DEDICATION

On August 9, 1959, the untimely death of John G. Kirkwood ended one of the most brilliant and productive careers in theoretical chemistry. Almost every field of physical chemistry has felt the impact of his work, which was powerful, incisive, and elegant. At the time of Professor Kirkwood's death,

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[1] Alfred P. Sloan Fellow.

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his major occupation was the theoretical study of transport processes, hence we believe it appropriate that this review be dedicated to his memory.

II. INTRODUCTION
II.1. DIRECTION

This review is limited to selected topics of the statistical theory of transport. Emphasis will be on the inter-relations between theories, the manner in which irreversibility is introduced, and the molecular interpretation of selected nonequilibrium processes. We mention, by reference only, the cluster theory of Montroll (1) and the Prigogine-Henin (2) analysis of the approach to equilibrium in crystals. We have made no attempt to hide our individual prejudices and preferences, for which we make no excuse. With the Editor's acquiescence we discuss in a moderately critical manner only the subjects that we consider of dominant importance. Our indebtedness to the literature and to the arguments of other investigators will be apparent at many points, but it is pertinent to mention that the Higgins' lectures of Professor G. E. Uhlenbeck (Princeton 1954) and numerous conversations with Professor J. E. Mayer have been of particular importance in shaping our ideas.

II.2. POINCARÉ CYCLES AND THEIR ESTIMATION

Among the valid characterizations of the behavior of bounded Newtonian mechanical systems of many degrees of freedom is the recurrence theorem of Poincaré (3, 29). Chandrasekhar (4) has reviewed the implications of this theorem for kinetic theory and statistical mechanics and has given a short demonstration of the theorem originally due to Zermelo (5). The theorem is stated by Chandrasekhar as follows: "In a system of material particles under the influence of forces which depend only on the spatial coordinates, a given initial state (given by a representative point in phase space) must, in general recur, not exactly, but to any desired degree of accuracy, infinitely often, provided the system always remains in the finite part of the phase space." This theorem has been the starting point for a number of "physical paradoxes" showing the supposed incompatability of statistical mechanics based on a dynamics that reveals a quasi-periodic character in the motion of the phase point and the predictions of kinetic theory and macroscopic thermodynamics [Zermelo (5)]. The resolution of these paradoxes by Boltzmann (6), von Smoluchowski (7), and others, have depended on the recognition that the average period of one such Poincaré cycle (for the usual macroscopic systems studied in statistical physics) is so very large that it is very improbable that a return of the system to the immediate vicinity of any initial state can be observed during the times normally available. This average time, of course, depends on the specification of the limits of error in a recurrence of a given state. Unfortunately, except for a rough estimate of this mean recurrence time for a gas by Boltzmann (6), no satisfactory demonstration of this reconciliation has been achieved. A very simple but crude estimate of the length of a recurrence time can easily be made for the dilute gas by noting that if the time between two collisions is about 10^{-12} seconds, the

total number of collisions per second in one mole of gas is about 10^{35}. This number must be compared with the total number of available states which is approximately $10^{10^{23}}$ so that the recurrence time becomes $10^{10^{23}}/10^{35} \approx 10^{10^{23}}$ sec.

Frisch (8) has recently attempted to elucidate certain details of this reconciliation suggested by Boltzmann, von Smoluchowski, and others, for at least a class of simple mechanical systems. These systems are the conditionally or multiply-periodic mechanical systems derivable from a time independent Hamiltonian. Introducing action and angle variables the characteristic frequencies ν_i, $i = 1, \cdots, N$, of the system of energy E are given by $\nu_i = \partial E/\partial J_i$, with J_i the ith action variable. Frisch, using certain results from the theory of diophantine approximations, suggested that the mean recurrence time T_{rec} for such systems is given, if $2\pi\epsilon$ is the error of the $\nu_i (0 < \epsilon < 1)$ allowed in the specification of the recurrent initial stage (the J_i are constants of the motion), by

$$T_{rec} \sim C_{NT}\epsilon^{-N} \qquad (\text{II}.2.1)$$

with $\tau^{-1} = \text{Max } \nu_i$ $(i = 1, \cdots, N)$ and C_N a constant not exceeding unity. He further investigates the question of what is the asymptotic fraction of the time, F, that a system is in a recurrent initial state. Using a theorem due to Weyl, it is found by Frisch that

$$F = \lim_{k \to \infty} \frac{N_1(\epsilon, t_k)}{t_k} = \epsilon^N \qquad (\text{II}.2.2)$$

provided only that $t_k \to \infty$ as $k \to \infty$. In Equation II.2.2, $t_k - t_{k-1}$ represents one of the time intervals during which such a multiply periodic system is under observation and $N_1(\epsilon, t_k)$ represents the sum of the time intervals during which the system is undergoing a recurrence to a given initial state. In turn, this result suggests that the fraction of the time such a system (starting from a given initial state) disobeys a strong version of the second law of thermodynamics is equal to or less than F.

An elegant and suggestive calculation of the mean recurrence time for a linear chain of N harmonically coupled mass points has been carried out by Hemmer, Maximon & Wergeland (9). Their result [given by their Equation (17)] illustrates quantitatively what was concluded on general grounds by Frisch (8), that $T_{rec} \sim \epsilon^{-N}$ (more accurately $\sim N^{-1}\epsilon^{2-N}$). A numerical example given by these authors indicates the enormity of these times even for relatively small systems and relatively broad error specification of the state; thus, for a chain of 10 mass points with a maximum frequency of 10 sec.$^{-1}$ and $\epsilon = \pi/100$ one finds $T_{rec} \sim 10^{10}$ years! Kac (10) has remarked that the result of Hemmer, Maximon & Wergeland follows very easily from a formula due to Smoluchowski. The problem of the distribution of recurrence times is important, since there may well be large fluctuations about the mean.

The quantum mechanical analog of the Poincaré recurrence has recently been formulated by Bocchieri & Loinger (11), as follows: "Consider a system with *discrete* energy eigenvalues E_n. If $\psi(t_o)$ is its state-vector in the Schröd-

inger picture at the time t_0 and ϵ is any positive number, at least one time T will exist such that the norm of the vector $\psi(T) - \psi(t_0)$ is less than ϵ." Furthermore, these authors show that this quantum recurrence theorem does not generally hold if the system has a continuous energy spectrum. The quantum systems having a continuous energy spectrum correspond to classical systems not bounded in a finite volume. This type of result has been used without proof in a number of investigations (e.g., Section IV).

II.3. Some General Aspects of Coarse Graining

The statistical mechanical theory of transport can be divided into two problems: the mechanism of the approach to equilibrium, and the relation of macroscopic fluxes to molecular properties. The first problem has long been investigated with the approach noted in Section II. 2; i.e., how do the reversible equations of mechanics lead to a description of irreversible phenomena? A possible resolution was suggested by Boltzmann, Smoluchowski and Ehrenfest, who indicated that for finite systems "true irreversibility" was to be replaced by "practical irreversibility." It was shown that the mean recurrence times for phase space configurations, differing more than infinitesimally from those most probable, were so large as to be unobservable. There is an approach to equilibrium on the human time scale even though, from the point of view of theoretical mechanics, Poincaré cycles exist for finite systems. In this, an apparent irreversibility exists only for times that are short relative to Poincaré cycles. But the reversibility of the basic laws of mechanics is more fundamental than this. Even though a realm of "practical irreversibility" is apparent, the problem of the approach to equilibrium remains unanswered.

To illustrate, consider a system containing N molecules. The positions and momenta of the molecules—with no internal freedoms—are specified by the $2N$ vectors $R_1, R_2 \cdots R_N, p_1, \cdots, p_N$. The normalized specific distribution function in the $6N$ dimensional phase space satisfies Liouville's equation

$$\frac{\partial f^{(N)}}{\partial t} + \sum_1^N \left[\frac{p_j}{m} \cdot \nabla_{R_j} f^{(N)} + (X_j + F_j) \cdot \nabla_{p_j} f^{(N)} \right] = 0 \qquad (II.3.1)$$

X_j is the external force acting on molecule j and F_j is the intermolecular force exerted on molecule j by the $N-1$ other molecules. This equation is equivalent to the equation of motion of an incompressible fluid with density $f^{(N)}$. The most general stationary density distribution is one for which $f^{(N)}$ is constant along streamlines. The quantity

$$H^{(N)} = \int f^{(N)} \ln f^{(N)} d\Omega \qquad (II.3.2)$$

therefore remains a constant along each streamline, and the entropy, customarily defined as $-kH^{(N)}$, also remains constant and does not approach the equilibrium value. Since $f^{(N)}$ remains constant if one moves with the "fluid," the distribution can only become uniform in a coarse-grained sense.

If the density is initially constant in different regions, then, because of the distortion of the streamlines due to streaming, the average density

$$\bar{\rho} = \Big(\prod_1^N \Delta\alpha_i \Big)^{-1} \int f^{(N)} d\alpha_1 \cdots d\alpha_N$$

over fixed regions will become equal. To show this, define

$$
\begin{aligned}
\mathrm{H}_{\bar{\rho}}^{(N)} &= \sum_m \bar{\rho}_m \ln \bar{\rho}_m (\Delta\alpha_1 \cdots \Delta\alpha_N)_m = \sum_m (\bar{\rho}_m \ln \bar{\rho}_m) \delta\tau_m \\
&= \int \bar{\rho} \ln \bar{\rho} d\alpha_1 \cdots d\alpha_N = \int f^{(N)} \ln \bar{\rho} d\alpha_1 \cdots d\alpha_N
\end{aligned}
\tag{II.3.3}
$$

$$
\begin{aligned}
dR_1 \cdots dR_N dp_1 \cdots dp_N &= \prod_1^N d\alpha_i \\
\delta\tau_m &= \Big(\prod_1^N \Delta\alpha_i \Big)_m
\end{aligned}
\tag{II.3.4}
$$

The symbol $\bar{\rho}_m$ represents the density in the mth cell of volume $\delta\tau_m$. We start with a non-uniform ensemble in which the density is actually constant in the set of regions $\delta\tau_1 \cdots \delta\tau_N$ so that at $t=0$ the fine grained and coarse grained densities are identical and

$$H^{(N)} = H_0^{(N)} = \int f^{(N)}(0) \ln f^N(0) d\alpha_1 \cdots d\alpha_N. \tag{II.3.5}$$

Now consider a later time t:

$$
\begin{aligned}
H_0^{(N)} - H_{\bar{\rho}}^{(N)}(t) &= \int [f^{(N)}(0) \ln f^{(N)}(0) - f^{(N)}(t) \ln \bar{\rho}(t)] d\alpha_1 \cdots d\alpha_N \\
&= \int [f^{(N)}(t) \ln f^{(N)}(t) - f^{(N)}(t) \ln \bar{\rho}(t) - f^{(N)}(t) + \bar{\rho}(t)] d\alpha_1 \cdots d\alpha_N
\end{aligned}
\tag{II.3.6}
$$

where the last two terms in the integrand sum to zero when integrated and we have used

$$
\begin{aligned}
\int f^{(N)} d\alpha_1 \cdots d\alpha_N &= \int \bar{\rho} d\alpha_1 \cdots d\alpha_N = 1 \\
\int f^{(N)}(t) \ln f^{(N)}(t) d\alpha_1 \cdots d\alpha_N &= \int f^{(N)}(0) \ln f^{(N)}(0) d\alpha_1 \cdots d\alpha_N
\end{aligned}
\tag{II.3.7}
$$

by the normalization conditions and Liouville's Theorem. Note that

$$F(x, y) = x \ln x - x \ln y - x + y \geq 0 \tag{II.3.8}$$

is only zero when $x = y$. Thus

$$H_0^{(N)}(t) - H_{\bar{\rho}}^{(N)}(t) \geq 0 \tag{II.3.9}$$

and $H_{\bar{\rho}}^{(N)}$ is smallest for the coarsely uniform ensemble.

This theorem, however, does not tell us which coarse grained density corresponds to our knowledge of an initial nonequilibrium situation. Uhlenbeck points out that this is connected with the difficulty of using an ensemble for the description of a single system and that the justification must lie in the

fact that a macroscopic description of a state corresponds to a very large number of microscopically different, but macroscopically indistinguishable, states (12). It must be assumed that the observed macroscopic changes of state are the same for the overwhelming majority of the members of the ensemble, so the time average of some quantity over the nonstationary ensemble will represent the change of the quantity with time for the single system. In terms of the derivation, there is no hint as to how to construct appropriate coarse-grained nonequilibrium ensembles. For sufficiently simple systems it is possible to introduce an explicit coarse graining by requiring an approach to equilibrium to occur in the sense of weak convergence only as has been done for multiply periodic systems (8a), or by using appropriate coarse-grained probability densities in phase space as investigated in certain one dimensional systems (8b). In both cases the approach to equilibrium can be interpreted as a Gibbs type stirring in phase space. Many divergences in he theory of transport begin when coarse graining is introduced.

The question of the appropriateness of coarse graining as a description of the approach to equilibrium must also be raised. Consider a monotonic entropy-time trajectory shown in Figure II.3.1. The time reversibility of
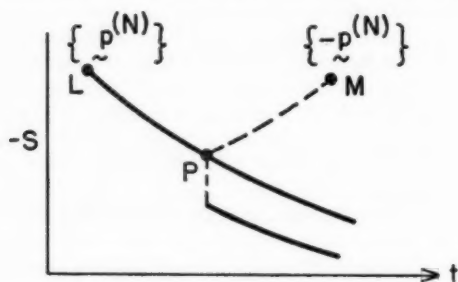
Fig. II.3.1

mechanical systems may be illustrated graphically by pointing out that if all momenta are reversed when the system is at point P on the entropy decay curve then the entropy will decrease along the dotted path PM. The usual interpretation of the Gibbs Theorem, as embodied in Equation II.3.9 is that coarse graining of the distribution function eliminates the possibility that a decrease in entropy can occur, even with momenta reversed. It appears to us that this argument is illusory and that the monotonic increase in entropy is generated by the coarse graining of the initial state. That is, the commitment to a distribution function averaged over a cell at $t=0$ introduces a large increase in entropy at $t=0$. This is shown in Figure II.3.1 by the displaced curve drawn as if the initial time were t_p and the distribution function were suddenly coarse grained. This entropy-time curve has the desired feature of monotonicity. It may be that the coarse graining procedure performs this feat by excluding all distribution functions of physical interest,

as suggested by the possibility of manufacturing spin echoes (13) or even negative temperatures (14, 15) in a decoupled system of nuclear spins. For such a system a fine-grained distribution function must be used to describe the approach to equilibrium.

II.4. Smoothing by Definition

The foregoing considerations suggest the question: "Is the mathematical smoothing introduced by the integration of an N-body distribution function sufficient to provide an irreversible approach to equilibrium?" The relevance of this question was indicated by Grad (50) whose work leads to the interesting idea that the entropy is greater when defined in terms of reduced distribution functions which do not satisfy a Liouville equation due to the interactions between particles. Even though $f^{(N)}$ is a constant in time, $f^{(1)}$ need not be, and therefore an entropy defined in terms of reduced distribution functions can show time dependence. It is a direct implication of this statement that the constancy of entropy, when defined as $-k \int f^{(N)} \ln f^{(N)} d\Omega$, is determined by very high order distribution functions and the complicated simultaneous correlations they describe. Some simple physical arguments serve to support but by no means prove this argument.

Grad's argument is of great interest and merits further examination. Consider the definitions

$$H^{(2)} = \int f^{(2)} \ln f^{(2)} f \Omega_{12}$$

$$\left.\begin{array}{l} H^{(1)}(1) \\ H^{(1)}(2) \end{array}\right\} \int \begin{array}{l} f^{(1)}(1) \ln f^{(1)}(1) d\Omega_1 \\ f^{(1)}(2) \ln f^{(1)}(2) d\Omega_2 \end{array} \tag{II.4.1}$$

with the usual normalization conditions

$$\int f^{(2)} d\Omega_{12} = \int f^{(1)}(1) d\Omega_1 = \int f^{(1)}(2) d\Omega_2 = 1$$

$$\int f^{(2)} d\Omega_1 = f^{(1)}(2) \tag{II.4.2}$$

$$\int f^{(2)} d\Omega_2 = f^{(1)}(1)$$

Then by simple subtraction

$$H^{(1)}(1) + H^{(1)}(2) - H^{(2)} = - \int f^{(2)} \ln f^{(2)} d\Omega_{12}$$

$$+ \int f^{(1)}(2) \ln f^{(1)}(2) d\Omega_2 + \int f^{(1)}(1) \ln f^{(1)}(1) d\Omega_1 \tag{II.4.3}$$

In the absence of interactions between the particles,

$$f^{(2)} = f^{(1)}(1) f^{(1)}(2) \tag{II.4.4}$$

and thereby

$$H^{(2)} = H^{(1)}(1) + H^{(1)}(2) \tag{II.4.5}$$

When there are interactions between the particles the pair distribution function is not the simple product of two singlet distribution functions. By introduction of a correlation function h_{12}, defined by the relation

$$h_{12} = f^{(2)} - f^{(1)}(1)f^{(1)}(2) \qquad (II.4.6)$$

it is easily seen that $h_{12} \to 0$ as the interaction tends to become vanishingly small. Now,

$$\int h_{12}d\Omega_{12} = \int f^{(2)}d\Omega_{12} - \int f^{(1)}(1)d\Omega_1 \int f^{(1)}(2)d\Omega_2 = 0 \qquad (II.4.7)$$

and the use of the mean value theorem leads to

$$\ln\left[f^{(1)}(1)f^{(1)}(2) + h_{12}\right] = \ln f^{(1)}(1)f^{(1)}(2) + \frac{h_{12}}{f^{(1)}(1)f^{(1)}(2) + \theta h_{12}} \qquad (II.4.8)$$

where θ is a real number between zero and unity. After direct substitution of II.4.8 into II.4.3 and some algebraic rearrangement it is found that

$$H^{(1)}(1) + H^{(1)}(2) - H^{(2)} = -\int h_{12}\left[1 + \frac{(1-\theta)h_{12}}{f^{(1)}(1)f^{(1)}(2) + \theta h_{12}}\right]d\Omega_{12} \qquad (II.4.9)$$

$$= \int \frac{(1-\theta)h_{12}^2}{f^{(1)}(1)f^{(1)}(2) + \theta h_{12}} \, d\Omega_{12} \geq 0$$

where the last form in Equation II.4.9 follows from the use of relation II.4.7. It is easily seen that the integrand of II.4.9 is always positive since both numerator and denominator are positive when $h_{12} \geq 0$ and when $h_{12} \leq 0$, $f^{(1)}(1)f^{(1)}(2) + \theta h_{12} \geq f^{(1)}(1)f^{(1)}(2) + h_{12} \geq 0$ since $h_{12} = f^{(2)} - f^{(1)}(1)f^{(1)}(2)$ and $0 \leq \theta \leq 1$. We have thereby established the interesting relationship

$$H^{(2)} \leq H^{(1)}(1) + H^{(1)}(2) \qquad (II.4.10)$$

and consequently the entropy is greater when defined in terms of reduced distribution functions.

To obtain a system displaced by $\Delta\mu(r)$ in chemical potential from the equilibrium value, by $\Delta T(r)$ in temperature, etc. we take the system of interest at equilibrium, and carefully observe it. Each time a spontaneous fluctuation creates the desired gradients, we freeze the system by suitable constraints. By repeating this procedure many times one can construct a fluctuation ensemble with the desired initial properties. Such a system is defined only by macroscopic properties. The initial state of the system may now be described by a grand partition function

$$\Xi = \sum_{\{N\}} \int \exp\left\{-\int \frac{e(r) - \sum N_i\mu_i(r)}{kT(r)} \, dr\right\} d\Omega \qquad (II.4.11)$$

where $e(r)$ is the energy density at r, $\mu_i(r)$ and $T(r)$ the chemical potential and temperature at r. It is important to emphasize that the ensemble so constructed is initially at local equilibrium because of the fluctuation path by which it was constructed. It is a nonequilibrium state only in the sense

that when the external constraints are removed, interactions with the surroundings will force a change in time back to the equilibrium state. These unspecified, and by implication, random interactions with the surroundings provide the mechanism by which the system is driven to equilibrium.

It is possible to extract some useful qualitative information from this formalism. First, since the system is initially in a state of local equilibrium it is implied that a finite time is required for the onset of the regression of the fluctuation. This finite time, in which transient behavior occurs, is not ordinarily described by the macroscopic laws of dissipative processes and it must be anticipated that it will be necessary to extrapolate the steady-state behavior in a manner which eliminates the lag period. Second, consider the difference in fluctuation paths in entropy-time variables, shown in Figure II.4.1, of two ensembles that have almost the same entropy. The curve NN
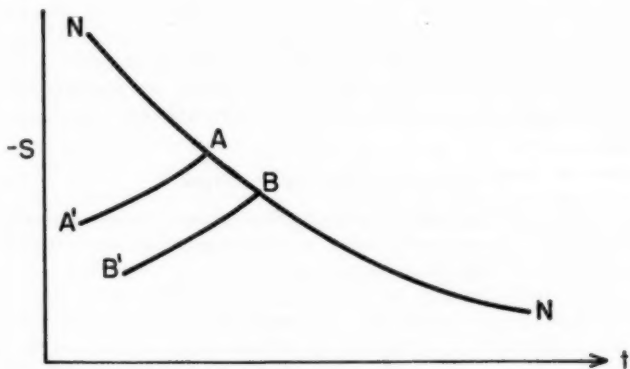
FIG. II.4.1

is to represent the path along which the negative entropy of an arbitrary fluctuation ensemble decays, different ensembles having different values of the initial entropy, say S_A and S_B, but all decaying along the same curve. An ensemble with entropy S_A will decay along AN for $t > 0$ and along AA' for $t < 0$, corresponding to the fact that the return to equilibrium is dissipative. Similarly, for an ensemble with entropy S_B two possible decay paths exist along BN and BB'. Consider now the difference between ensembles A and B. If the curve NBA is traversed in the right to left direction, the difference between ensembles A and B only becomes evident at the point where the curve BB' branches off. System A "remembers" a collision history of greater extent than system B and hence will go further along to more negative entropies. It is instructive to estimate the magnitude of the number of collisions "remembered." If all collisions were distinct and no two molecules collided twice, the number of collisions in time Δt would be of

order $2^{\Delta t/t_c}$ where t_c is the time between collisions. A more realistic estimate suggests that a molecule must be mechanically correlated in time Δt with all other particles in the volume

$$\frac{4\pi}{3}\left(\lambda_f \frac{\Delta t}{t_c}\right)$$

where λ_f is a mean free path. For a gas t_c is of the order of 10^{-12} sec. Thus, even in the very short time interval of $\Delta t = 10^{-10}$ sec. the number of collisions that must be "remembered" for the system to reverse its mechanical trajectory lies in the range 8×10^{11} to 10^{80}. The net result of this calculation is the conclusion that for a system to decrease its entropy in a macroscopic process, correlated motions involving very large numbers of molecules are always necessary. For very short times by macroscopic standards, the required correlations are of such a high order as to be of no interest for the calculation of mechanical or thermodynamical functions. This introduces a practical irreversibility different from that discussed previously. Though the irreversibility apparently arises from the correlation times, its origin is in the macroscopic nature of the interactions between system and surroundings that make possible the use of the fluctuation ensemble and grand partition function.

II.5. THE MASTER EQUATION

Two conjectural approaches to nonequilibrium processes are, respectively, the attempt to construct general nonequilibrium ensembles, and the approximation embodied in the Master equation.

The theoretical construction of nonequilibrium ensembles is largely due to Lebowitz & Bergmann (16, 17). The program is essentially designed to develop a statistical-mechanical theory of nonequilibrium processes, motivated by the success of the statistical mechanics of Gibbs for the equilibrium state. A single parameter, the temperature, completely describes the phase-space ensemble representing a closed system in equilibrium. While undoubtedly no such simple characterization is possible when a system is not in equilibrium, it would be of great value if we could use the methods of statistical mechanics, i.e., the construction of phase-space ensembles, for studying such systems.

The principles of Gibbsian statistical mechanics have been successfully applied to systems not far from equilibrium. To cite a few examples: Onsager's reciprocal relations (18, 27) and Callen's fluctuation dissipation theorem (19, 19a, 19b), are built on the concepts of statistical mechanics. Prigogine *et al.* (20, 42) go even further in investigating both heat conduction in crystals and the statistical mechanical origins of irreversibility. These results were achieved without developing a complete statistical mechanics of nonequilibrium processes. In attempting to develop such a theory, one encounters the difficulty that in order for a system to approach a steady state, or to remain in a nonequilibrium stationary state, it cannot be isolated but must be in contact with surroundings (reservoirs) which maintain gradients within

it. Moreover, in order for the process to be truly stationary, these reservoirs must be inexhaustible and have an infinite number of degrees of freedom. The difficulty lies in finding a phase-space that will describe this system plus reservoir combination.

Lebowitz and Bergmann overcome this difficulty by constructing a model reservoir that, as far as the system is concerned, always has the same appearance and consists of an infinite number of independent, identical components, each of which interacts with the system but once. It is further assumed that there is an impulsive interaction between system and reservoir components. Hence, the effect of the reservoir on the system can be completely described if the time-independent distribution of reservoir components in the μ-space of the reservoir before collision is specified; it is never necessary to deal with the total, infinite, phase-space of the reservoir. These reservoirs are the statistical-mechanical counterpart of thermodynamic temperature baths. The ensemble, representing a system in contact with such reservoirs, obeys an integro-differential equation in Γ-space, containing both the Liouville equation and a stochastic integral term that describes the collisions with the reservoirs. Lebowitz & Bergmann (16, 17) explored some of the consequences of this model and found that if a stationary solution— i.e., a stationary ensemble—exists it will be unique and will be approached asymptotically by every time-dependent solution. In general, the stationary state is not an equilibrium state; the ensemble remains unchanged only because its surroundings maintain temperature gradients inside the system. Only if these surroundings are all at one temperature, i.e., if the system is in contact with but one reservoir, will the stationary state correspond to the canonical distribution. In the presence of several reservoirs at slightly different temperatures, the Onsager reciprocal relations were shown to be satisfied by the stationary distribution. In this model the Onsager relations are thus obtained without any reference to fluctuation theory and without the assumption of detailed balancing.

Recently, Lebowitz & Frisch (21) studied in detail the behavior of a simple nonequilibrium ensemble, one representing a Knudsen gas in a container whose walls are maintained at different temperatures. They were able, for that system, to derive an iteration procedure for finding the stationary distribution. Also, an explicit stationary solution was found for the case where an accommodation coefficient completely characterizes the effect of gas collisions with the wall. Separately, Gross & Lebowitz (22) examined some aspects of the quantum theory of a system interacting impulsively with a reservoir at temperature T. Equations analogous to those derived in reference (16) for the classical distribution function were postulated for the quantum density operator of such a system. These equations were then applied to the quantum theory of dielectric relaxation. Still more recently, Lebowitz (23) has extended the previous work by finding exact stationary nonequilibrium solutions for some simple systems, and has introduced a simple relaxation-type method for finding approximate stationary solutions for the distribution function.

Aside from the discussion of Brownian motion problems (24), the general theory of Lebowtiz and Bergmann has not been applied to physical problems. In particular, the utility of this approach for the discussion of transport phenomena in dense media remains subject to the difficulty of handling in detail the interactions between the system and reservoir. It is amply clear that the element of irreversibility enters in the assumed stochastic interactions at the walls, and this underlies the difference between the Lebowitz-Bergmann approach and that based on the Master equation. As will be seen, the Master equation is an irreversible description of motion in Γ space standing intermediate in complexity between the full description afforded by the rigorous time-reversible Liouville equation and the partial description of a system in μ-space afforded by the Boltzmann equation. Since the Master equation occupies an intermediate position it is clear that there must be a large number of such equations. The brief analysis to follow will be simple in form. We shall not discuss at this time the problem of multiple random phasing (25) and refer the reader to Sections III.3 and IV.2 for more sophisticated analyses.

Consider a spatial homogeneous dilute gas in the absence of external forces. A $3N$ dimensional velocity vector V may be formed from the N velocity vectors $p_1/m, \cdots, p_N/m$. Now consider a process in which a collision occurs in the time interval dt between the ith and j^{th} molecules. Let the line of centers of molecules i and j be in the range l to $l+dl$. Kac (25) assumes that the probability of such a collision is

$$\psi_{ij}dldt = \psi\left(\left[\frac{p_j}{m} - \frac{p_i}{m}\right]\cdot l, \left|\frac{p_j}{m} - \frac{p_i}{m}\right|\right)dldt$$

$$= \frac{\sigma^2}{v}\frac{\left|\left[\frac{p_j}{m} - \frac{p_i}{m}\right]\cdot l\right| - \left[\frac{p_j}{m} - \frac{p_i}{m}\right]\cdot l}{2}$$

(II.5.1)

with the second form valid for rigid spheres of diameter σ. Due to the collision between molecules i and j the Master velocity vector V is altered such that

$$V' = A_{ij}(l)V$$

$$A_{ij}(l)V = \left[\frac{p_1}{m}, \cdots \frac{p_i}{m} + \left[\frac{p_j}{m} - \frac{p_i}{m}\right]\cdot ll, \cdots \frac{p_j}{m}\right.$$

$$\left. - \left[\frac{p_j}{m} - \frac{p_i}{m}\right]\cdot ll, \cdots, \frac{p_N}{m}\right].$$

(II.5.2)

Thus $V \to V'$ with probability $\psi_{ij}dldt$ and $V' \to V$ with probability

$$1 - dt\sum_{1\leq i<j\leq N}\psi_{ij}\,dl.$$

The conditions of constant total momentum and constant total energy imply that V describes a $3N-3$ dimensional sphere. Let the initial distribu-

tion of velocities correspond to a distribution of points on the surface of the sphere, $\phi(V, 0)$. Then this distribution function will evolve as

$$\frac{\partial \phi(V, t)}{\partial t} = \sum_{1 \leq i < j \leq N} \int dl [\phi(A_{ij}(l)V, t) - \phi(V, t)] \psi_{ij}. \qquad (\text{II}.5.3)$$

This is the Master equation in which the analogue of the Stosszahlansatz is embodied in the assumed form for ψ_{ij}, and is interesting in that it is linear and thereby differs considerably from the Boltzmann equation. For a simplified form of Equation II.5.3, Kac has shown that if the distribution function $\phi(V, 0)$ is initially factorized, i.e., initially a product of one molecule distribution functions, then this property of factorization is preserved for all time. A completely general proof of this propagation property has not been published. We note that the physical picture underlying the derivation is that of a random walk of the vector on the surface of the sphere of constant total energy. In a certain sense, the assumption of a random walk on the surface of constant energy is equivalent to an averaging of the distribution function over cells with dimensions of the order of magnitude of the average jump length. In a sense, this kind of random motion is related to an ill-defined coarse graining. In view of the form of Equation II.5.3 and the physical picture to which it corresponds it is not surprising that it is possible to demonstrate an H-theorem for factorizable distribution functions.

The chief disadvantages of the Master equation lie in the apparent impossibility of extending it to the case where streaming of the gas occurs, the extreme difficulties encountered in the treatment of strongly interacting systems, and the complete lack of discussion of the mechanical nature of the assumption embodied in Equation II.5.1. These topics will be considered in succeeding sections, and we now turn to a unifying analysis of the arguments of this general section.

II.6. MAYER'S THEOREM

The considerations of the preceding sections may be codified and organized with the aid of an important theorem due to Mayer (26).

Consider the distinction between mechanical reversibility and thermodynamic reversibility. For the purpose of our argument we define mechanical reversibility in an overly restrictive manner so as to remove all the "gray" aspects of the problem. Consider a system of particles subject to some external forces. Let the forces be varied slowly so that after a suitable elapsed time the external constraints are identical with those acting initially on the system. The set of external forces has put the system through a cyclic variation. If, at the end of this variation, the position and momentum of each particle is identical with the initial position and momentum, then we shall say that such a system is mechanically reversible.

Consider now a system composed of a tenuous gas enclosed in a cylinder with frictionless piston. Let the piston be cycled slowly until the initial volume is again attained. If this process is sufficiently slow the thermody-

namic state of the gas is the same at the end of the cycle as at the start and the process is thermodynamically reversible. But it is evident that the positions and momenta of the molecules of the gas are very likely completely different before and after the cycle, hence only certain aspects of the distribution of positions and momenta are reversible. This system is therefore thermodynamically reversible but not mechanically reversible in the restrictive sense of our definition.

The distinction we have just drawn forms the underlying basis of many of the arguments of the preceding sections. This is perhaps most easily seen in quantum mechanical terms. In a system in which the number of particles is small and the spacing of energy levels sufficiently large, mechanical reversibility is attainable. In a system in which the number of particles is very large, it is ordinarily true that the spacing of the energy levels is so small that, for all practical purposes, no matter how slowly we actually perform a cyclic variation of the state of the system the final state is mechanically different from the initial state, even though the final and initial states may be thermodynamically identical. Thus the expansion of a gas on the time scale of hours permits an uncertainty in energy of the order of 10^{-30} ergs, a quantity enormously larger than the separation of translational levels in an ideal gas ($\sim 10^{-10^{22}}$ ergs or less).[2]

With the preceding arguments we are led to conclude that for any macroscopic process the best one can hope to achieve is thermodynamic reversibility, but never mechanical reversibility within the scope of our definition. The fact that the fundamental equations of mechanics are time reversible is of secondary importance with relation to macroscopic dissipation. In particular, the solution of the Liouville equation or its quantum mechanical counterpart must show that for any process in a macroscopic system proceeding at a finite rate, irreversibility is present. That is, Liouville's equation already involves the necessary elements of irreversible behavior and additional hypotheses such as coarse graining or random phasing are not necessary. The actual use of coarse graining or random phasing may then be interpreted as mathematical devices suitable for the selection of certain spectral ranges responsive to specific experiments, and more rapid phenomena must be discussed by other techniques, or the use of shorter coarse graining intervals.

[2] This estimate is easily made for an ideal gas by recognizing that

$$\Delta E = \frac{dE}{d\Omega} = kTe^{-S/k}$$

since

$$\frac{d\Omega}{dE} = \frac{de^{S/k}}{dE} = \frac{1}{kT}e^{S/k}$$

with Ω the number of states with energy less than or equal to E. Since $kT \sim 10^{-14}$ ergs at room temperature and $e^{-S/k} \sim e^{-N}$, we obtain the quoted result, $\Delta E \sim 10^{-10^{22}}$.

To quantify the preceding arguments we must recognize that the known properties of the system require a given set of distribution functions $f^{(n)}$, for small numbers of molecules, $n < n_0$. Now, an ensemble of classical systems is mechanically defined in all detail by giving the probability density in Γ space. In an ensemble of open systems, $f^{(N)}$ must be given for all $N \geq 0$. Consistent with the observation that only a few low-order distribution functions determine the state of the system for all macroscopic purposes, we note that $f^{(N)}$ is uncertain except that its contraction must give the proper $f^{(1)}, f^{(2)}, f^{(3)}, \cdots$ that is, there is an infinite continuum of functions $f^{(N)}$ consistent with the available macroscopic information. Consider functions $f_G^{(N)}(v, \lambda, \{N\})$ defined for an open system and which may depend upon a parameter λ. The probability that exactly N molecules are in v is

$$P^N(v, \lambda) = \frac{1}{N!} \int f_G^{(N)}(v, \lambda, \Omega_N) d\Omega_N \tag{II.6.1}$$

$$\sum_{N \geq 0} \frac{1}{N!} \int f_G^{(N)}(v, \lambda, \Omega_N) d\Omega_N \equiv 1 \tag{II.6.2}$$

and the reduced probability densities $f^{(n)}(v, \lambda, \Omega_n)$ are likewise defined by

$$f^{(n)}(v, \lambda, \Omega_N) = \sum_{N \geq 0} \frac{1}{N!} \int f_G^{(N+n)}(v, \lambda, \Omega_{N+n}) d\Omega_N$$
$$f^{(0)} = 1. \tag{II.6.3}$$

Now differentiate Equation II.6.3 with respect to λ,

$$\frac{\partial f^{(n)}}{\partial \lambda} = \sum_{N \geq 0} \frac{1}{N!} \int \frac{\partial f_G^{(N+n)}}{\partial \lambda} d\Omega_N \tag{II.6.4}$$

$$\frac{\partial^2 f^{(n)}}{\partial \lambda^2} = \sum_{N \geq 0} \frac{1}{N!} \int \frac{\partial^2 f_G^{(N+n)}}{\partial \lambda^2} d\Omega_N \tag{II.6.5}$$

and necessarily $\partial f^{(0)}/\partial \lambda = \partial^2 f^{(0)}/\partial \lambda^2 = 0$. Consider a set of correlation functions defined in terms of $f_G^{(\nu)}$ for $0 \leq \nu \leq n$ by

$$\phi_n = \sum_{\nu=0}^{n} \sum_{\{\nu\}_n} (-)^{n-\nu} \ln f_G^{(\nu)}(v, \lambda, \Omega(\{\nu\}_n)) \tag{II.6.6}$$

where, for a given set of ν molecules, the sum runs over all $n!/\nu!(n-\nu)!$ different subsets $\{\nu\}_n$ of numbered molecules of the numbered set n. By inversion,

$$\ln f_G^{(N)} = \sum_{n=0}^{N} \sum_{\{n\}_N} \phi_n(v, \lambda, \Omega(\{n\}_N)). \tag{II.6.7}$$

At equilibrium, the entropy is defined by

$$-\frac{S}{k} = \sum_{N \geq 0} \frac{1}{N!} \int f_G^{(N)} \ln f_G^{(N)} d\Omega_N \tag{II.6.8}$$

and Mayer uses this as a general definition for *any* ensemble. Differentiation with respect to λ gives

$$-\frac{1}{k}\frac{\partial S}{\partial \lambda} = \sum_{N\geq 0}\frac{1}{N!}\int \frac{\partial f_G^{(N)}}{\partial \lambda}(\ln f_G^{(N)} + 1)d\Omega_N = \sum_{N\geq 0}\frac{1}{N!}\int \frac{\partial f_G^{(N)}}{\partial \lambda}\ln f_G^{(N)}d\Omega_N \quad \begin{matrix}(\text{II}.6.9)\\(\text{II}.6.10)\end{matrix}$$

$$-\frac{1}{k}\frac{\partial^2 S}{\partial \lambda^2} = \sum_{N\geq 0}\frac{1}{N!}\int\left[\frac{\partial^2 f_G^{(N)}}{\partial \lambda^2}(\ln f_G^{(N)} + 1) + \frac{1}{f_G^{(N)}}\left(\frac{\partial f_G^{(N)}}{\partial \lambda}\right)^2\right]d\Omega_N \quad (\text{II}.6.11)$$

$$= \sigma + \sum_{N\geq 0}\frac{1}{N!}\int \frac{\partial^2 f_G^{(N)}}{\partial \lambda^2}\ln f_G^{(N)}d\Omega_N \quad (\text{II}.6.12))$$

$$\sigma = \sum_{N\geq 0}\frac{1}{N!}\int\left[\frac{\partial \ln f_G^{(N)}}{\partial \lambda}\right]^2 f_G^{(N)}d\Omega_N. \quad (\text{II}.6.13)$$

Since $f_G^{(N)}$ is by definition always positive, the quantity $\sigma \geq 0$.

Now we seek to express the derivatives of S in terms of the correlation functions defined above. By substitution of the summation expansions of each of the derivatives it is found that

$$-\frac{1}{k}\frac{\partial S}{\partial \lambda} = \sum_{n\geq 1}\frac{1}{n!}\int \phi_n \frac{\partial f^{(n)}}{\partial \lambda}d\Omega_n \quad (\text{II}.6.14)$$

$$-\frac{1}{k}\frac{\partial^2 S}{\partial \lambda^2} = \sigma + \sum_{n\geq 1}\frac{1}{n!}\int \phi_n \frac{\partial^2 f^{(n)}}{\partial \lambda^2}d\Omega_n. \quad (\text{II}.6.15)$$

Now define

$$\phi_n(v, \lambda = 0, \Omega_n) = \phi_n^\circ \quad (\text{II}.6.16)$$

and define further

$$\phi_n^\circ = 0; \quad n \geq n_o \quad (\text{II}.6.17)$$

Assume arbitrary functions $\phi_n(v, \lambda, \Omega_n)$ for $n \geq n_o$ consistent with the condition II.6.17 that they be identically zero when $\lambda = 0$. The functions $\phi_n(v, \lambda, \Omega_n)$ for $n \geq n_o$ may be fixed such that

$$\frac{\partial f^{(n)}}{\partial \lambda} = \frac{\partial^2 f^{(n)}}{\partial \lambda^2} = 0, \quad n < n_o. \quad (\text{II}.6.18)$$

where this may be done using the general integral equation relations of Mayer.

With the use of II.6.17 and II.6.18, the sums displayed in II.6.14 and II.6.15 are both zero at $\lambda = 0$, since $\phi_n = 0$ for $n \geq n_o$, and the derivatives are zero for $n < n_o$. Thus the entropy is an extremum at $\lambda = 0$. By virtue of the sign of the second derivative, this extremum is a maximum. Thus it has been proved that the function $f_G^{(N)}$ that has maximum entropy consistent with a fixed set of n_o reduced distribution functions, $f^{(1)}, f^{(2)}, \ldots, f^{(n_o-1)}$ is that function for which $\phi_n = 0$ if $n \geq n_o$.

In physical terms it has been shown that the entropy is maximized by the "smoothest" probability density consistent with given restraints. The function $f_G^{(N)}$ for $\lambda \neq 0$ contains correlation functions $\phi_n(n \geq n_o)$ giving detailed correlations in phase space between numbers, n, of molecules. At $\lambda = 0$ these correlations are wiped out, but in such a way that their averaged effect is retained by altering the correlations $\phi_n(n < n_o)$ so as to retain the same physical characteristics of the ensemble in the unaltered $f^{(n)}$ for $n < n_o$). The entropy is a maximum for the "smoothed" functions.

In the usual transport problem, at $t=0$ the system is described by an ensemble representing local thermodynamic equilibrium. Equation II.6.8 then gives the correct initial entropy. If the ensemble were to be represented by hypothetical completely isolated systems, then $f_G^{(N)}(t)$ is determined by $f_G^{(N)}(0)$ from the Liouville equation. Moreover, as discussed previously, the correlation functions ϕ_n for large numbers of molecules grow with time until, in an ordinary system, only a millisecond is required to effect correlations involving all the molecules in the system. This corresponds to the fact that $\partial S/\partial t$ is zero for an isolated system. Real systems are always in some sort of container, and very small time-dependent container fluctuations will destroy the high order correlations; but if the systems by definition behave as thermodynamically isolated systems then the mechanical properties will be those predicted for isolated systems: the functions $f^{(n)}(v, t, \Omega_n)$ for $n \leq n_o$ will be those computed from the correlation functions $\phi_n(v, t, \Omega_n)$ of the ensemble of strictly isolated systems. The actual correlation functions for large n will be wiped out by the fluctuations, but those for small n will be altered by this "smoothing" so as to retain the $f^{(n)}$ of the isolated ensemble. The course of the negative entropy as a function of time can therefore be described as a flow into the high order correlation functions, followed by a destruction there due to the otherwise trivial time dependent random fluctuations introduced at the walls.

The Mayer formulation in no way deals with the mechanical aspects of irreversibility. In this theorem the irreversibility enters at the "walls" through the use of the Grand Ensemble to describe the behavior of the system. In this sense the theorem is only partially complete, since a description of the stochastic nature of the wall interactions would be of interest. It may be possible to combine the approaches of Mayer and of Lebowitz & Bergmann (17) to permit joint discussion of the stochastic wall interactions and the many body distribution functions.

III. GENERAL THEORIES

III.1. KIRKWOOD'S THEORY

The approach to a theory of transport in dense media proposed by Kirkwood (28) is based in part upon analogies with the theory of Brownian motion. It is therefore pertinent to examine briefly the mechanical behavior of a Brownian particle.

Consider a massive particle immersed in a medium composed of small molecules. The equation of motion of the massive particle, according to Langevin's formulation (4), is represented as

$$m \frac{d^2R}{dt^2} + \zeta \frac{dR}{dt} = \mathbf{X}(t) \tag{III.1.1}$$

with ζ a frictional coefficient and $\mathbf{X}(t)$ a fluctuating force that gives rise to the irregular motion of the particle. An alternative formulation starts from the notion of transition probabilities. Let $K^{(1)}(R_2 t_2/R_1 t_1)$ be the conditional probability density that a Brownian particle which was at the point R_1, at

time t_1 will be at R_2 at time t_2. Regarding the Brownian motion as a stationary Markoff process requires that

$$K^{(1)}(R_3 t_2/R_1 t_1) = \int K^{(1)}(R_3 t_2/R_3 t_3)K^{(1)}(R_3 t_3/R_1 t_1)dR_3 \qquad \text{(III.1.2)}$$

$$t_2 > t_3 > t_1$$

and

$$K^{(1)}(R_2 t_2/R_1 t_1) = \sum_n u_n(R_2)e^{-\lambda_n(t_2-t_1)}v_n^*(R_1) \qquad \text{(III.1.3)}$$

where u_n and v_n^* are the eigenfunctions and λ_n the nth eigenvalue of the Fokker-Planck operator describing the time rate of change of the initial and final states, respectively. Now, starting from the diffusion equation, Einstein (30) showed that the transition probability $K^{(1)}$ was given by

$$K^{(1)}(R_2/R_1; s) = \frac{\exp\left\{-(R_2 - R_1)^2/4\mathcal{D}s\right\}}{(4\pi\mathcal{D}s)^{3/2}} \qquad \text{(III.1.4)}$$

$$s = t_2 - t_1$$

a result which may be physically interpreted as a statement of the central limit theorem since the net displacement $R_2 - R_1$ is visualized as the resultant of numerous elementary displacements arising from the rapidly fluctuating force $X(t)$. Moreover, since $X(t)$ itself is the resultant of the superposition of numerous random forces, the central limit theorem suggests that the probability density for finding a force of magnitude X is proportional to $\exp\left(-X^2/4kT\zeta\right)$ with the factor $4kT\zeta$ determined by the condition that the distribution of the velocities of the Brownian particles be Maxwellian after a sufficiently long time.

In the description of Brownian motion based upon transition probabilities the irreversibility enters in the assumption that the process is stationary and Markoffian. This assumption places a set of restrictions on the fluctuating force $X(t)$ in the Langevin formalism. These conditions are:

(a) The average of $X(t)$ over an ensemble or over a long period of time vanishes,

$$\langle X(t)\rangle = 0.$$

(b) There is no correlation between the fluctuation forces at two different times,

$$\langle\langle X t_1)X(t_2)\rangle = \langle X^2\rangle\delta(t_2 - t_1)$$

and $\langle X^2\rangle$ is independent of time.

(c) The description of the Brownian motion as a function of time requires the solution of Equation III.1.1 for long times, and the rejection of the solution for short times. For, in very short time intervals, the mean square particle displacement is,

$$\langle(R_2 - R_1)^2\rangle = c_o^2 s^2;$$

(s very small) where c_o is the initial velocity. This result expresses the fact that the influence of the immediately preceding dynamical event persists for times that are short compared to the time between events. It may readily

be shown that the solution of Equation III.1.1 for times long compared to the time between dynamical events leads to the identification

$$\mathfrak{D} = \frac{kT}{\zeta} = \frac{\langle (R_2 - R_1)^2 \rangle}{6s} \tag{III.1.5}$$

after direct comparison of the two formulations discussed above. The conclusion to be drawn is that the description of Brownian motion as a stationary Markoff process requires discussion of the average motion during the period of time of length τ. The interval τ must be chosen so as to render the basic dynamical event stochastically independent of both prior and future events.

We now turn to a discussion of the rate of change of the distribution function for a set of molecules. Liouville's equation, II.4.1, may be integrated to yield

$$\left.\begin{aligned}
\frac{\partial f^{(1)}}{\partial t} + \frac{p_1}{m} \cdot \nabla_{R_1} f^{(1)} + X_1 \cdot \nabla_{P_1} \bar{f}^{(1)} &= \nabla_{P_1} \cdot (N-1) \Omega^{(1)} \\
\Omega^{(1)} &= -\frac{1}{\tau} \int_0^\tau \int F_{12} f^{(N)} (R_1 R_2 p_1 p_2 \zeta P : t + s) dQ dP dp_2 dR_2 ds \\
\bar{f}^{(n)} &= \frac{1}{\tau} \int_0^\tau \int f^{(N)} (R^{(n)} p^{(n)} R^{(N-n)} p^{(N-n)}; t+s) dR^{(N-n)} dp^{(N-n)} ds
\end{aligned}\right\} \tag{III.1.6}$$

where the time coarse graining clearly indicates that we seek an averaged description in the sense just defined for Brownian motion. Just as in the case of Brownian motion it is convenient to describe the time rate of change of the various phase densities by the use of transition probabilities. The phase space transformation function $K^{(N,N)}(R^{(N)} p^{(N)} / R^{(N)'} p^{(N)'}; s)$ is the conditional probability density of finding the coordinates $R^{(N)} p^{(N)}$ after an interval s, given that the original coordinates were $R^{(N)'} p^{(N)'}$. Therefore

$$f^{(N)}(R^{(N)} p^{(N)}; (t+s)$$

$$= \int K^{(N,N)}(R^{(N)} p^{(N)} / R^{(N)} p^{(N)'}; s) f^{(N)}(R^{(N)}, p^{(N)} ; t) dR^{(N)} dp^{(N)} \tag{III.1.7}$$

and it may easily be shown that $K^{(N,N)}$ satisfies the Liouville equation with initial condition

$$K^{(N,N)}(R^{(N)} p^{(N)} / R^{(N)'} p^{(N)} ; 0) = \prod_{i=1}^N \delta(R_i - R_i')\delta(p_i - p_i') \tag{III.1.8}$$

To obtain the form of the transition probability it is convenient to use a perturbation expansion in which the force term in the Liouville equation is replaced by $\lambda(F_i + X_j)$ with λ a small parameter. Representation of the solution as a power series in λ leads to the first approximation (31)

$$K_1^{(N,N)} = -\sum_{j=1}^N \Delta p_j^{(1)}(s) \cdot \nabla_{p_j} \left\{ \prod_{k=1}^N \delta \left(R_k - R_k' - s\frac{p_k}{m} \right) \delta \left(p_k - p_k' \right) \right.$$

$$\Delta p_j^{(1)}(s) = \int_0^s \left[F_j \left(R' + s'\frac{p_j}{m} \right) + X_j \left(R_j' + s'\frac{p_j}{m} \right) \right] ds' \tag{III.1.9}$$

$$\Delta R_j^{(1)}(s) = \frac{s p_j}{m}$$

with $\Delta R_j^{(1)}(s)$ the distance traversed by a free particle in time s, $F_j\left(R' + s'\frac{p_j}{m}\right)$ the force on the particle traveling along a linear trajectory and $\Delta p_j^{(1)}(s)$ the change in momentum due to this particular force. The increments in coordinates and momenta displayed are the first terms in the development in powers of λ, of ΔR_j and Δp_j obtained from an exact solution of the equations of motion. Corresponding to Equation III.1.4 we have to order λ^2

$$K^{(N,N)}(R^{(N)}p^{(N)}/R^{(N)\prime}p^{(N)\prime}; s)$$

$$= \left[1 - \lambda \sum_1^N \Delta p_j^{(1)}(s) \cdot \nabla_{P_j}\right] \prod_1^N \delta(R_k - R_k' - \Delta R_k^{(o)})\delta(p_k - p_k') \tag{III.1.10}$$

Equation III.1.10 may now be substituted into Equation III.1.7. The N body distribution function is then related to the singlet distribution function by the definition (58)

$$^{(N)}(R_1R_2p_1p_2QP; t)$$

$$= g^{(2)}(R_1R_2p_1p_2; t)f^{(2/N-2)}(R_1R_2p_1p_2/QP; t) \times f^{(1)}(R_1p_1; t)f^{(1)}(R_2p_2; t) \tag{III.1.11}$$

where $f^{(2/N-2)}$ is the relative probability density in the subspace QP given that molecules one and two have specified coordinates and momenta, and $g^{(2)}$ is the pair correlation function. If it is now assumed that: (a) the environment of particles one and two is in statistical equilibrium, (b) the pair correlation function can be approximated by its equilibrium value, and (c) the dependence of $f_o^{(2/N-2)}$ [where the subscript (o) indicates the equilibrium value] on p_1' and p_2' is neglected when differentiation with respect to these variables is performed; then, the distribution function in singlet space satisfies the Fokker-Planck equation in phase space (28)

$$\frac{\partial f^{(1)}}{\partial t} + \frac{p_1}{m} \cdot \nabla_{R_1} f^{(1)} + \nabla_{P_1} \cdot (F_1^* + X_1) f^{(1)} = \nabla_{P_1} \cdot \zeta_1 \left[\frac{p_1}{m} f^{(1)} + kT\Delta_{P_1} f^{(1)}\right]$$

$$\zeta_1 = \frac{N-1}{3kT\tau} \int_o^\tau \int_{-s}^o \int F_{12} F_1 \left(R + (s+s')\frac{p}{m}\right) f_o^{(1/N-1)}(R_1p_1/QP) dPdQdsds'. \tag{III.1.12}$$

The quantity ζ_1 is seen to be a friction constant which by virtue of III.1.12 is related to the intermolecular forces.

Although the derivation sketched depends upon the neglect of terms of order $(\Delta p)^2$ and is therefore valid for systems in which the particle under consideration suffers small momentum changes in the interval τ, it must not be concluded that the equation may not have a considerably greater range of validity. The situation is analogous to the derivation of the Navier-Stokes equation from the kinetic theory of dilute gases. Such a derivation cannot be taken to imply that the Navier-Stokes equation is applicable only to dilute gases and not to dense fluids. In each case sufficient conditions have been found to derive the relevant equations, but the investigation of the *necessary* conditions for the derivation remains incomplete.

The determination of the coefficients of shear and bulk viscosity and of

thermal conduction proceed from Equation III.1.12 and the similar equation for the distribution function in pair space. In each case moments are obtained by multiplying the variable into the appropriate Fokker-Planck equation and averaging, followed by the identification of coefficients with those in the phenomenological Newtonian stress tensor and Fourier heat flux. In all of this work it is assumed that the frictional coefficient is independent of momentum and of time (plateau value). The agreement with experiment is heartening in view of the difficulty of the calculations and will be examined in more detail in a later section.

To conclude this brief exposition of the Kirkwood theory we wish to draw attention to the marked difference in form between Equations III.1.4 and III.1.9. The discrepancy, which has interesting physical overtones, may be further explored by the following. Define (32)

$$B_t(\Delta t) = \int_t^{t+\Delta t} X(t)dt \cong X(t)\Delta t \tag{III.1.13}$$

and by condition (b) on the fluctuation force,

$$\langle B_t^2 \rangle = \int_t^{t+\Delta t}\int \langle X(t)X(s)\rangle dt ds = X^2\Delta t \tag{III.1.14}$$

and the distribution of $B_t(\Delta t)$ is Gaussian for the reasons cited previously. Thus the probability density for $B_t(\Delta t)$ is proportional to $\exp(-B_t^2/4kT\zeta\Delta t)$. But for Δt very small the path of a Brownian particle is determined by specifying $X(\Delta t)$ with a probability density given as above. By convolution, the probability of a path from t_1 to t_2 is given by

$$P(B_{t_1})P(B_{t_1+\Delta t})\cdots P(B_{t_2-\Delta t}) \propto \exp\left\{-\sum B_t^2/4kT\zeta\Delta t\right\} \tag{III.1.15}$$

and in the limit as $\Delta t \to 0$,

$$\lim_{\Delta t \to 0} P(B_{t_1})\cdots P(B_{t_2-\Delta t}) \propto \exp\left\{-\int_{t_1}^{t_2} X^2(t)dt/4kT\zeta\right\}. \tag{III.1.16}$$

Thus if $X(t)$ is specified for all values of t in the range $t_1 \leq t \leq t_2$ and the initial conditions are given, the path of the Brownian particle is determined. The transition probability is obtained from III.1.16 and is

$$K^{(1)}(R_2t_2/R_1t_1) = A\int \exp\left\{-\frac{\int_{t_1}^{t_2} X^2(t)dt}{4kT\zeta}\right\} d(\text{path}) \tag{III.1.17}$$

a path integral given by Onsager & Machlup (33). As usual, A is a normalization constant. When the inertia term in the Langevin equation can be neglected, Equation III.1.17 reduces to

$$K^{(1)}(R_2t_2/R_1t_1) = A\int \exp\left\{-\frac{\int_{t_1}^{t_2}\left\{\dfrac{dR}{dt}\right\}^2 dt}{4\mathfrak{D}}\right\} d(\text{path}) \tag{III.1.18}$$

which can be shown to lead to the uncertainty relation

$$\langle \Delta p \rangle \langle \Delta q \rangle \cong 2m\mathfrak{D} \qquad (\text{III}.1.19)$$

Thus, by virtue of III.1.5 the instantaneous velocity of the Brownian particle cannot be defined, and by III.1.19 the resultant uncertainty in velocity is related to the diffusion coefficient and the corresponding uncertainty in position. Both of these results are characteristic of the necessity for coarse graining in time, or solving Equation III.1.1 only for long times.

In contrast, Equation III.1.9 represents an accurate mechanical solution subject only to the mathematical approximations of perturbation theory. Since the theory is classical in the mechanical sense, both position and momentum can be precisely defined simultaneously. It is only after insertion of III.1.9 or III.1.10 into III.1.17 and the operations indicated that the coarse graining in time converts the reversible mechanical description to the dissipative representation embodied in the Fokker-Planck equation. The differences in form between III.1.4 and III.1.9 are therefore directly related to the method of introducing the element of irreversibility. In a later section we shall consider the question of the utility of an approximation in which a molecule follows a diffusive trajectory with $K^{(1)}$ given by an equation of the form of III.1.4 rather than the linear trajectory form, III.1.9.

III.2. DISSIPATION-FLUCTUATION RELATIONS

The spirit of the fluctuation-dissipation approach, as exemplified in the work of Kubo (34), is the development of generalized relations for kinetic coefficients without the detailed use of molecular dynamics but with the use of the laws of general dynamics. The method used is to treat the response of a system to an external force by a perturbation method. At first we restrict attention to external disturbances which can be expressed as an extra term in the Hamiltonian, thus omitting heat flow or mass flow under gradients of temperature or chemical potential. These topics will be considered separately.

We consider our system to be subjected to an external force $F(t)$ of dynamical nature which may be represented as an additional term in the Hamiltonian. Thus

$$H = H_o + H_{\text{ext}}$$
$$H_{\text{ext}} = -AF(t) \qquad (\text{III}.2.1)$$

The distribution function for the system, $f^{(N)}$, satisfies the equation of motion

$$\frac{\partial f^{(N)}}{\partial t} = -\sum_{p,q}\left(\frac{\partial f^{(N)}}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial f^{(N)}}{\partial p}\frac{\partial H}{\partial q}\right) \qquad (\text{III}.2.1)$$

Now assume that the perturbation of the distribution function created by $F(t)$ is small and write

$$f^{(N)} = f_o{}^{(N)} + \Delta f^{(N)} \qquad (\text{III}.2.3)$$

whereby

$$\frac{\partial f_o{}^{(N)}}{\partial t} = 0 = - \sum_{p,q} \left(\frac{\partial f_o{}^{(N)}}{\partial q} \frac{\partial H_o}{\partial p} - \frac{\partial f_o{}^{(N)}}{\partial p} \frac{\partial H_o}{\partial q} \right). \qquad \text{(III.2.4)}$$

The substitution of III.2.1 and III.2.3 into III.2.2 gives

$$
\begin{aligned}
\frac{\partial \Delta f^{(N)}}{\partial t} &= - \sum \left(\frac{\partial \Delta f^{(N)}}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial \Delta f^{(N)}}{\partial p} \frac{\partial H}{\partial q} \right) \\
&\quad + F(t) \sum \left(\frac{\partial f^{(N)}}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial f^{(N)}}{\partial p} \frac{\partial A}{\partial q} \right) \\
&= - i\mathcal{L}^{(N)} \Delta f^{(N)} + F(t) \sum \left(\frac{\partial f^{(N)}}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial f^{(N)}}{\partial p} \frac{\partial A}{\partial q} \right)
\end{aligned} \qquad \text{(III.2.5)}
$$

which defines the linear operator $\mathcal{L}^{(N)}$ as

$$i\mathcal{L}^{(N)} g = - \sum \left(\frac{\partial g}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial g}{\partial p} \frac{\partial H}{\partial q} \right). \qquad \text{(III.2.6)}$$

If there were no external forces, the phase point $(q_o p_o)$ at time zero would go over to the phase point (qp) at time t. From Equations III.2.6 and III.2.2 we see that in such a natural motion

$$e^{-it\mathcal{L}^{(N)}} A(p_o, q_o) = A(p, q) \qquad \text{(III.2.7)}$$

where $A(p, q)$ is any dynamical quantity, and for which we also have the equation of motion

$$\frac{dA}{dt} = - \sum \left(\frac{\partial A}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial A}{\partial p} \frac{\partial H}{\partial q} \right). \qquad \text{(III.2.8)}$$

If it is assumed that $F(-\infty) = 0$ and, therefore, $\Delta f^{(N)}(-\infty) = 0$, then Equation III.2.5 may be formally integrated to give

$$\Delta f^{(N)}(t) = \int_{-\infty}^{t} e^{i(t-t')\mathcal{L}^{(N)}} \sum \left(\frac{\partial f^{(N)}}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial f^{(N)}}{\partial p} \frac{\partial A}{\partial q} \right) F(t') dt' \qquad \text{(III.2.9)}$$

Consider now the expectation value of an arbitrary quantity B which is given by

$$\langle B(t) \rangle = \int B f^{(N)}(t) d\Omega \qquad \text{(III.2.10)}$$

where $d\Omega$ is the volume element in the complete phase space. In terms of the perturbation expansion

$$
\begin{aligned}
\langle \Delta B(t) \rangle &= \int B \Delta f^{(N)}(t) d\Omega \\
&= \int_{-\infty}^{t} dt' \int d\Omega B e^{i(t-t')\mathcal{L}^{(N)}} \sum \left(\frac{\partial f^{(N)}}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial f^{(N)}}{\partial p} \frac{\partial A}{\partial q} \right) F(t') \\
&= \int_{-\infty}^{t} dt' F(t') \int \sum \left(\frac{\partial f^{(N)}}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial f^{(N)}}{\partial p} \frac{\partial A}{\partial q} \right) B(t - t') d\Omega.
\end{aligned} \qquad \text{(III.2.11)}
$$

Formally, a response function $\phi_{BA}(t)$ which describes the response of the system apparent in B by application of a unit pulse may be defined as

$$
\begin{aligned}
\phi_{BA}(t) &= \int \sum \left(\frac{\partial f^{(N)}}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial f^{(N)}}{\partial p} \frac{\partial A}{\partial q} \right) B(t) d\Omega \\
&= \int f^{(N)} \sum \left(\frac{\partial B}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial B}{\partial p} \frac{\partial A}{\partial q} \right) d\Omega
\end{aligned}
\tag{III.2.12}
$$

so that

$$
\langle \Delta B(t) \rangle = \int_{-\infty}^{t} \phi_{BA}(t - t') F(t') dt'.
\tag{III.2.13}
$$

The physical interpretation of III.2.11 is that the response $\Delta B(t)$ is a superposition of the effects of pulses $F(t')dt'$, $-\infty < t' < t$. The response function, defined for a unit pulse, is then integrated over time and may be considered to be an after effect function. Note that III.2.11 results from the relations

$$
\begin{aligned}
\int d\Omega B e^{i(t-t')} \mathcal{L}^{(N)} &\sum \left(\frac{\partial f^{(N)}}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial f^{(N)}}{\partial p} \frac{\partial A}{\partial q} \right) \\
&= \int d\Omega(p_o, q_o) B(p_o, q_o) \sum \left(\frac{\partial f^{(N)}}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial f^{(N)}}{\partial p} \frac{\partial A}{\partial q} \right)_{(q, p)} \\
&= \int d\Omega(q, p) B(p, q) \sum \left(\frac{\partial f^{(N)}}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial f^{(N)}}{\partial p} \frac{\partial A}{\partial q} \right)_{(q_o, p_o)} \\
&= \int d\Omega(q_o, p_o) B(p, q) \sum \left(\frac{\partial f^{(N)}}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial f^{(N)}}{\partial p} \frac{\partial A}{\partial q} \right)_{(q_o, p_o)}
\end{aligned}
\tag{III.2.14}
$$

since

$$
d\Omega(q_o, p_o) = d\Omega(q, p)
\tag{III.2.15}
$$

We may re-express the content of Equation III.2.12 as follows. The quantity

$$
- \sum \left(\frac{\partial f^{(N)}}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial f^{(N)}}{\partial p} \frac{\partial A}{\partial q} \right)
\tag{III.2.16}
$$

is the change in the distribution function due to a pulse. The effect of this pulse on the average value of the dynamical function B at a later time is given by III.2.12 in the first line. However, instead of inquiring about the change in distribution function we may also think of the effect of the pulse on the equation of motion of B. The second line of III.2.12 represents this outlook.

If $f^{(N)}$ is of the form

$$
f^{(N)} = C e^{-H/kT}
\tag{III.2.17}
$$

Then

$$
\sum \left(\frac{\partial f^{(N)}}{\partial q} \frac{\partial A}{\partial p} - \frac{\partial f^{(N)}}{\partial p} \frac{\partial A}{\partial q} \right) = \frac{1}{kT} \frac{dA}{dt} f^{(N)}
\tag{III.2.18}
$$

and thereby

$$\phi_{BA}(t) = \frac{1}{kT} \langle \dot{A}(o)B(t) \rangle = -\frac{1}{kT} \langle A(o)\dot{B}(t) \rangle \qquad \text{(III.2.19)}$$

where we have used the condition

$$\frac{d}{dt} \langle A(t)B(t + \tau) \rangle = 0 \qquad \text{(III.2.20)}$$

We should point out that the relationship between $\langle \Delta B \rangle$ and the response function is valid even when the initial distribution is very peaked. Such exceptional initial states correspond to very large fluctuations from equilibrium and though $\langle \Delta B \rangle$ is defined, we have no way of obtaining $\Delta f^{(N)}$ for such cases.

Let us now consider the special case of a periodic disturbance,

$$F(t) = F_o e^{i\omega t} \qquad \text{(III.2.21)}$$

For this periodic force, the response is

$$\langle \Delta B(t) \rangle = Re \left[F_o e^{i\omega t} \int_o^\infty \phi_{BA}(t) e^{-i\omega t} dt \right] \qquad \text{(III.2.22)}$$

If we consider the disturbance to have been switched on adiabatically in the infinite past, we may write

$$F(t) = \lim_{\epsilon \to +0} F_o e^{i\omega t + \epsilon t} \qquad \text{(III.2.21')}$$

and define an admittance function

$$\begin{aligned}
\chi_{BA}(t) &= \int_o^\infty \phi_{BA}(t) e^{-i\omega t} dt = \lim_{\epsilon \to +0} \int_o^\infty \phi_{BA}(t) e^{-i\omega t - \epsilon t} dt \\
&= \lim_{\epsilon \to +0} \frac{1}{\epsilon + i\omega} \left[\phi_{BA}(o) + \int_o^\infty \phi_{BA}(t) e^{-i\omega t - \epsilon t} dt \right] \qquad \text{(III.2.23)} \\
&= \Phi_{BA}(o) - i\omega \int_o^\infty \Phi_{BA}(t) e^{-i\omega t} dt
\end{aligned}$$

by partial integration. The relaxation function $\Phi_{BA}(t)$ is defined by

$$\Phi_{BA}(t) = \int_t^\infty \phi_{BA}(t') dt' \qquad \text{(III.2.24)}$$

By using Equation III.2.19

$$\Phi_{BA}(t) = \frac{1}{kT} \langle AB(t) - \bar{A}\bar{B} \rangle \qquad \text{(III.2.25)}$$

where $\bar{A}$ and $\bar{B}$ are the time averages

$$\bar{A} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_o^\tau A(t) dt \qquad \text{(III.2.26)}$$

and represent the invariant portions of A and B with respect to the natural motions of the system. Note that $\Phi_{BA}(t)$ as defined goes to zero as t tends to infinity or it oscillates. In any event, it has no constant contribution. Also note that since $\Phi_{BA}(t) = \Phi_{BA}(-t)$ then $\Phi_{BA}(t)$ is a real function.

We may summarize these considerations by saying that the linear response of a dynamical quantity $B(p, q)$ to an external force $F(t)$ is representable as the superposition of after effects corresponding to successive responses to unit impulses.

As an application, consider the problem of electrical conductance. For an electric field $E(t)$, the perturbation energy is taken as

$$H_{\text{ext}} = - \sum_i e_i r_i \cdot E(t) \tag{III.2.27}$$

with r_i the position vector of charge e_i. Substitution of III.2.27 into III.2.12 gives for the current flow in the μ direction when an electric field is applied in the ν direction

$$\phi_{\mu\nu}(t) = \int d\Omega \left(\frac{\partial \sum e_i x_{i\nu}}{\partial p} \frac{\partial f^{(N)}}{\partial q} - \frac{\partial \sum e_i x_{i\nu}}{\partial q} \frac{\partial f^{(N)}}{\partial p} \right) J_\mu(t) \tag{III.2.28}$$

where the current is

$$J_\mu = \sum_i e_i \dot{x}_{i\mu} \tag{III.2.29}$$

If the system has unit volume, the conductance tensor $\sigma_{\mu\nu}$ for a periodic field is given by

$$\sigma_{\mu\nu}(\omega) = \int_o^\infty e^{-i\omega t} dt \int d\Omega \left(\frac{\partial \sum e_i x_{i\nu}}{\partial p} \frac{\partial f^{(N)}}{\partial q} - \frac{\partial \sum e_i x_{i\nu}}{\partial q} \frac{\partial f^{(N)}}{\partial p} \right) J_\mu(t) \tag{III.2.30}$$

where we have used the admittance function defined in III.2.23 in accord with the Ohm's law relation between conductance (admittance) and field. The static conductance is obviously

$$\begin{aligned}
\sigma_{\mu\nu}(0) &= \int_o^\infty dt \int d\Omega \left(\frac{\partial \sum e_i x_{i\nu}}{\partial p} \frac{\partial f^{(N)}}{\partial q} - \frac{\partial \sum e_i x_{i\nu}}{\partial q} \frac{\partial f^{(N)}}{\partial p} \right) J_\mu(t) \\
&= \lim_{\epsilon \to +0} \frac{1}{\epsilon} \left[\phi_{\mu\nu}(0) + \int_o^\infty \dot{\phi}_{\mu\nu} e^{-\epsilon t} dt \right]
\end{aligned} \tag{III.2.31}$$

We may evaluate the expression in brackets in Equation III.2.28 to obtain

$$\sum_{p,q} \left(\frac{\partial \sum e_i x_{i\nu}}{\partial p} \frac{\partial f^{(N)}}{\partial q} - \frac{\partial \sum e_i x_{i\nu}}{\partial q} \frac{\partial f^{(N)}}{\partial p} \right) = - \sum_i e_i \frac{\partial f^{(N)}}{\partial p_{i\nu}} \tag{III.2.32}$$

and thereby

$$\phi_{\mu\nu}(0) = \int d\Omega f^{(N)} \sum_i \sum_j e_i e_j \frac{\partial}{\partial p_{i\nu}} \dot{x}_{j\mu}(0) = \int d\Omega f^{(N)} \sum_i e_i^2 \frac{\delta_{\mu\nu}}{m_i} = \sum_i \frac{N_i e_i^2}{m_i} \tag{III.2.33}$$

since the vector potential in which the electron moves is independent of momentum. The last expression in III.2.33 results from the normalization of $f^{(N)}$ to the total number of particles.

Suppose now that the distribution function in momentum space is at local equilibrium, i.e.,

$$f^{(N)} = h(q) \exp \left\{ - \sum_i p_i^2 / 2mkT \right\} \tag{III.2.34}$$

Then the use of Equation III.2.32 followed by explicit differentiation of II.2.34 and integration of III.2.31 gives

$$\sigma_{\mu\nu} = \frac{Ne^2}{kT} \int_o^\infty \langle u_\nu(o) u_\mu(t) \rangle dt \qquad \text{(III.2.35)}$$

with u_μ the component of average velocity in the μ direction. Consider the charged particles to be non-interacting. Then

$$\lim_{t \to \infty} \langle u_\nu(o) u_\mu(t) \rangle = 0 \qquad \text{(III.2.36)}$$

and we can write

$$\int_o^\infty \langle u_\nu(o) u_\mu(t) \rangle dt = \lim_{\tau \to \infty} \frac{1}{2\tau} \int_o^\tau \int_o^\tau \langle u_\nu(t') u_\mu(t) \rangle dt dt'$$
$$= \lim_{\tau \to \infty} \frac{1}{2\tau} \langle (x_\nu(\tau) - x_\nu(o))(x_\mu(\tau) - x_\mu(o)) \rangle = \mathfrak{D}_{\mu\nu} \qquad \text{(III.2.37)}$$

where $\mathfrak{D}_{\mu\nu}$ is the diffusion coefficient. Combination of III.2.37 and III.2.35 yields

$$\sigma_{\mu\nu} = \frac{Ne^2 \mathfrak{D}_{\mu\nu}}{kT}, \qquad \text{(III.2.38)}$$

the well known Einstein relation.

The treatment of the flows resulting from nonmechanical forces requires some new considerations. We shall follow closely the theory given by Mori (35). Consider a nonequilibrium liquid in contact with heat and mass reservoirs. The equilibrium state which the liquid approaches we describe with the grand ensemble probability density

$$P_o{}^{(N)} = \frac{\exp \left\{ -\frac{1}{kT_0} \left[H - \sum N_i \mu_{io} \right] \right\}}{\Xi_0} \qquad \text{(III.2.39)}$$

The nonequilibrium state changes in time, with the time rate of change determined by the Hamiltonian H and the interactions with the reservoirs. The decay to equilibrium will be assumed to occur via local equilibrium states specified by local temperatures $T(r)$ and local chemical potentials $\mu_i(r)$. This means that the system decays along the curve described in Section II.3 and may be considered to be describable by fluctuation ensemble. In the usual way, the average value of any dynamical quantity F is given by

$$\langle F(t) \rangle = \frac{1}{\Xi} \int \sum_{\{N\}} F(t) \exp \left\{ -\int \frac{1}{kT(r)} [e(r) - \sum N_i \mu_i(r)] dr \right\} d\Omega_N \qquad \text{(III.2.40)}$$

Assume now that the liquid deviates but slightly from equilibrium, that is from the local equilibrium ensemble, and express the probability density in the form

$$P_i{}^{(N)} = \frac{\exp \left\{ -\frac{1}{kT_o} [H - \sum N_i \mu_{io} + R] \right\}}{\Xi} \qquad \text{(III.2.41)}$$

In order to eliminate the initial lag period introduce a time smoothing operation

$$\frac{\delta}{\delta t} \langle F(t) \rangle = \frac{1}{\tau} \int_0^\tau ds \frac{d}{ds} \langle F(t+s) \rangle \tag{III.2.42}$$

and by rearrangement and partial integration

$$\frac{\delta}{\delta t} \langle F(t) \rangle = \frac{d}{dt} \langle F(t) \rangle + \int_0^\tau ds \left[1 - \frac{s}{\tau} \right] \frac{d^2}{ds^2} \langle F(t+s) \rangle \tag{III.2.43}$$

from which is obtained

$$\frac{\delta}{\delta t} \langle F(t) \rangle = \langle \dot{F}(t) \rangle - \int_0^\tau ds \left(1 - \frac{s}{\tau} \right) \phi_{\dot{F}\dot{R}} \tag{III.2.44}$$

where $\phi_{AB}(s)$ is the correlation function introduced previously

$$\phi_{\dot{F}\dot{R}}(s) = -\frac{1}{kT} \langle \dot{F}(t)\dot{R}(t+s) \rangle \tag{III.2.45}$$

Now assume that F vanishes for times shorter than t so that

$$\frac{\delta}{\delta t} \langle F(t) \rangle = \langle \dot{F}(t) \rangle + \int_0^\tau \phi_{\dot{R}\dot{p}}(s) ds \tag{III.2.46}$$

The term $\dot{R}$ arises from the coupling of the uniformization in coordinate space with the relaxation within the local regions. We have

$$\dot{R} = -\sum \left(\frac{\partial R}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial R}{\partial p} \frac{\partial H}{\partial q} \right) = \int \frac{T_\bullet}{T(r)} [e(r) - \sum \mu_i(r) n_i(r)] dr \tag{III.2.47}$$

which expresses $\dot{R}$ in terms of the time rate of local changes due to H.

$$\rho_i(r) = \sum_i m_i \delta(r_i - r)$$

$$N_i = \int n_i(r) dr = \int \sum_i \delta(r_i - r) dr \tag{III.2.48}$$

and the momentum density is

$$j_i(r) = \sum p_i \delta(r_i - r) \tag{III.2.49}$$

To obtain the overall densities of mass and momentum, sum over all components. Obviously, the macroscopic local mass velocity is

$$u(r,t) = \frac{\langle j(r,r) \rangle}{\langle \rho(r,t) \rangle} \tag{III.2.50}$$

and the internal energy density

$$e(r) = H(r) - j(r) \cdot u + \tfrac{1}{2} \rho u \cdot u \tag{III.2.51}$$

with $H(r)$ the local Hamiltonian

$$H = \int H(r) dr = \sum_i \int \left[\frac{p_i(r) \cdot p_i(r)}{2m} + X_i + \sum_{i \neq j} u_{ij} \right] dr \tag{III.2.52}$$

We now turn to the development of expressions for the transport coefficients. Since

$$\dot{r}_i = p_i/m_i$$
$$\dot{p}_i = \sum_{i \neq j} F_{ij} = -\sum_{i \neq j} \nabla_{r_i} u_{ij} \qquad \text{(III.2.53)}$$

we can easily obtain the ordinary continuity equations. The procedure is to define each time derivative as the divergence of a flow and then use the general dynamical equations to evaluate the time derivative in terms of the quantities in III.2.53. By identification of coefficients it is possible to obtain a molecular definition of the transport coefficients. The essential feature involved in the evaluation of the transport coefficients is the use of explicit relations derived from the macroscopic theory of irreversible processes. Thus, from the relation between the diffusion coefficient and the entropy production in a diffusing system, by evaluation of the entropy flux as above, the diffusion coefficient is calculated. Following this idea put

$$\dot{\rho}_i = -\nabla \cdot j_i$$
$$\dot{\rho} = -\nabla \cdot j$$
$$H = -\nabla \cdot J_H \qquad \text{(III.2.54)}$$
$$j = -\nabla \cdot J_j$$

In this way one finally obtains for, say, the coefficient of shear viscosity

$$\eta = \frac{1}{v} \int_0^\tau ds \langle \mathcal{G}_V^{zv}(t) \mathcal{G}_V^{zv}(t+s) \rangle$$
$$\mathcal{G}_V = \sum_i \left[\frac{p_i p_i - \langle p_i p_i \rangle}{m_i} \right] + \frac{1}{2} \sum_{i \neq j} \sum [F_{ij} r_{ij} - \langle F_{ij} r_{ij} \rangle] \qquad \text{(III.2.55)}$$

where $\mathcal{G}_V$ is itself an average over a volume V, sufficiently large to contain many molecules but small compared with the total volume of the fluid.

It is readily seen that the intent of theory based on a fluctuation ensemble is to provide molecular expressions for the transport coefficients in terms of the time fluctuations of the dynamical fluxes in equilibrium. The irreversible terms in the hydrodynamic equations, namely the thermodynamic fluxes, are the sums of the products of the correlation functions of the dynamical fluxes and the affinities, and thereby connect the uniformization in coordinate space to the processes represented by the time dependence of the correlation functions of the dynamical fluxes. Although molecular expressions have been obtained, the theory is clearly semi-macroscopic in nature. In particular, irreversibility enters directly at the point where the higher terms in the perturbation expansion are dropped, as well as where the relations III.2.54 are assumed.

In view of the importance of these relations between correlation functions and macroscopic transport coefficients it is pertinent to re-examine the derivation from a point of view closer to that expressed earlier. Kirkwood (36)

has provided just such an analysis and we shall follow his alternative derivation in all details.

Kirkwood's point of departure is the Liouville equation, which can be written in the form

$$\mathscr{L}^{(N)}f^{(N)} = -i\frac{\partial}{\partial t}f^{(N)}$$

$$\mathscr{L}^{(N)} = i\left[\sum \frac{p_j}{m}\cdot\nabla_{R_j} + F_j\cdot\nabla_{P_j}\right] \tag{III.2.56}$$

with $\mathscr{L}^{(N)}$ a self-adjoint operator. We consider as equilibrium distribution function, $\bar{f}_{eq}^{(N)}$, the canonical distribution of Gibbs. The distribution function $\bar{f}^{(N)}$ will be written as the sum of a zero order function $\bar{f}_o^{(N)}$ (which is, in general, different from the equilibrium function) and a perturbation term $\bar{f}_1^{(N)}$. The purpose of the development is to examine the equation for $\bar{f}_1^{(N)}$ induced by the Liouville equation. As before we consider only linear terms in the deviations from equilibrium in this equation. Thus, Kirkwood's procedure exactly parallels the Chapman-Enskog treatment of the Boltzmann equation.

The deviation from equilibrium will be measured by r parameters, γ_k, for example the rate of shear and the temperature gradient.

Quite generally, $\bar{f}^{(N)}$ can be divided according to

$$\bar{f}^{(N)} = f_o^{(N)}(\gamma_1, \cdots \gamma_r) + \bar{f}_1^{(N)} \tag{III.2.57}$$

with

$$\bar{f}_1^{(N)} = \sum_1^r \bar{f}_{1k}^{(N)}\gamma_k \tag{III.2.58}$$

There is considerable freedom in the choice of $\bar{f}_o^{(N)}$. It must, of course, reduce to the equilibrium distribution $\bar{f}_{eq}^{(N)}$ when each of the parameters γ_k vanishes. Otherwise, the motivation for a choice of $\bar{f}_o^{(N)}$ is only convenience. For viscous flow and for heat flux it is convenient to choose a pseudo-canonical distribution.

In the linear approximation, in which terms quadratic in the deviations (γ_k) from equilibrium are neglected, the equation for $\bar{f}_1^{(N)}$ takes the form

$$\mathscr{L}^{(N)}\bar{f}_1^{(N)} + i\frac{\partial}{\partial s}\bar{f}_1^{(N)} = iB\bar{f}_{eq}^{(N)} \tag{III.2.59}$$

where s is the time variable and $s = 0$ at the time t when the perturbation described below is turned on. Here B (and B_k) is defined by the equations

$$\mathscr{L}^{(N)}\bar{f}_o^{(N)} = -iB\bar{f}_{eq}^{(N)} = -i\sum_1^r \gamma_k B_k\bar{f}_{eq}^{(N)} \tag{III.2.60}$$

After a long time the system will relax to the equilibrium distribution and since there are no stationary deviations from equilibrium there is no nontrivial stationary solution to III.2.60. Thus, we must seek to describe decay

to equilibrium rather than seek a stationary solution. Still another aspect of the triviality of stationary solutions is that for such solutions, the Liouville equation would take the form

$$\mathcal{L}^{(N)}\bar{f}_{stat}^{(N)} = 0$$

so that $\bar{f}_{stat}^{(N)}$ could be a function only of the dynamical invariants. The number of such invariants is generally quite small (except in highly non-ergodic systems such as coupled harmonic oscillators). In any case distribution functions having this property could not consistently describe transport processes.

Kirkwood solves the inhomogeneous equation for $\bar{f}_1^{(N)}$ by expanding it in terms of (properly normalized) eigenfunctions of the Liouville operator,

$$\mathcal{L}^{(N)}\phi_k = \lambda_k \phi_k \tag{III.2.61}$$

$$\bar{f}_1^{(N)} = \sum_k \bar{f}_{1k}^{(N)}(s)\phi_k \tag{III.2.62}$$

where use has been made of the self-adjointness of $\mathcal{L}^{(N)}$ and the notation Σ_k symbolically represents summation over the discrete spectrum (if any) of $\mathcal{L}^{(N)}$ and integration over its continuous spectrum.

Suppose that the perturbation is turned on at time t; that is, that the temperature T and velocity u were uniform before that time. Kirkwood then seeks an expression for $\bar{f}_1^{(N)}$ as a function of the time variable s.

Combining Equations III.2.59 and III.2.62 and using the ortho-normality of the ϕ's,

$$i\frac{d\bar{f}_{1k}^{(N)}}{ds} + \lambda_k \bar{f}_{1k}^{(N)}(s) = i\langle B\phi_k^*\rangle_{eq} = i\int B\bar{f}_{eq}^{(N)}\phi_k^* d\Omega \tag{III.2.63}$$

for $s > 0$.

This equation can easily be integrated. The evaluation of average values of functions of dynamical variables that are induced by the integral of this equation can be expressed according to

$$\langle\psi\rangle = \langle\psi\rangle^{(o)} + \langle\psi\rangle^{(1)} \tag{III.2.64}$$

where $\langle\psi\rangle^{(o)}$ represents the contribution from averaging over the distribution $\bar{f}_o^{(N)}$, while $\langle\psi\rangle^{(1)}$ is given by

$$\langle\psi\rangle^{(1)} = -\int_o^\tau \langle\psi(t)B(t+s)\rangle_{eq} ds \tag{III.2.65}$$

One should note at this point that $\langle\psi\rangle^{(o)}$ need not vanish; whether it does or not depends upon the choice of $\bar{f}_o^{(N)}$. In general in the linear approximation

$$\langle\psi\rangle^{(o)} = \langle\psi\rangle_{eq} + \left\langle \psi \sum_1^\tau \lambda_k \frac{d\ln\bar{f}_o^{(N)}}{d\lambda_k}\right\rangle \tag{III.2.66}$$

From Equations III.2.64, III.2.66, and III.2.65 we may obtain expressions for the heat flux and stress tensor. For $\bar{f}_o^{(N)}$ choose a velocity distribu-

tion Gaussian about the mean hydrodynamic velocity and take the local temperature for the temperature parameter in this distribution. Thus,

$$\bar{J}_o^{(N)} = A \exp \left\{ - \sum_1^N \frac{(p_j - mu)^2}{2mkT_j} - \frac{1}{k} \sum_{i<j} \frac{2u_{ij}}{T_i + T_j} \right\} \qquad \text{(III.2.67)}$$

with A a normalization constant. We may now compute B. It can be written as the sum of terms proportional to the various parameters γ_k according to

$$B = \frac{1}{kT} \left[S:\nabla u + Q \cdot \nabla \ln T \right] \qquad \text{(III.2.68)}$$

If this expression is introduced into Equation III.2.65, one obtains the following expression for the heat conductivity κ:

$$\kappa = \frac{1}{kT} \int_o^\tau \langle Q_i \cdot Q_{i+s} \rangle_{eq} ds \qquad \text{(III.2.69)}$$

It is not immediately clear from the derivation that these integrals, which are the final results, make sense. For if τ becomes large, the integrals vanish so long as we are dealing with a canonical ensemble. In order for the expressions to have meaning, it is necessary that a time scale exist that is long by molecular standards and short compared to microscopically significant times, such that the η and κ, identified above, are essentially time-independent over this scale. Lacking a proof of the existence of such a time scale, these Kubo relations cannot be considered to have been completely justified.

III.3. VAN HOVE, BROUT, PRIGOGINE

The preceding section dealt with the effects of external disturbances. For closed systems the outstanding problems of statistical mechanics are those that arise when we consider the temporal evolution of isolated mechanical systems of many degrees of freedom subject to perturbations arising from the mutual interactions between the degrees of freedom of the system. If H is the part of the total Hamiltonian characterizing the unperturbed system, and λV the perturbation, then the total Hamiltonian can be written as $H + \lambda V$ where λ is a dimensionless parameter characterizing the size of the perturbation. As long as we are not interested in studying specific surface effects it may suffice to study the behavior of these systems in the limit where both the number of degrees of freedom, characterized by a number N (e.g., in a many particle system N is the number of particles), and the volume of the system, v, are allowed to approach infinity in such a way that the ratio N/v, the concentration, remains finite. This limiting condition should suffice to eliminate the problems raised by the existence of Poincaré cycles in finite, bounded mechanical systems. One expects a basic dichotomy in the behavior of the perturbed motion of these systems: the first is associated with the many-particle systems usually studied in statistical mechanics, in which the perturbed motion possesses a dissipative character which leads to an irreversible approach to thermodynamic equilibrium for almost all initial unperturbed

states of the system.[3] Well-known examples of such perturbations are the interaction between phonons in crystals, the interaction between electrons and phonons in crystalline conductors, the intermolecular forces in imperfect gases, etc. The second kind of basic behavior is exhibited in the interactions between quantized fields, in which the perturbed motion is free of such a dissipative character for a finite fraction of initial unperturbed states of the system; for example, the interaction between a free electron field and a free photon field, etc. We shall speak of the first class of perturbations as statistical-mechanical and of the second class as field-theoretical.

Many questions arise which deal with the nature and effects of the statistical-mechanical perturbations: (a) What common characteristic properties can be isolated which lead to irreversible effects? (b) What is the time dependence of the transition probability, in a given time interval, between suitably chosen groups of unperturbed stationary states; more definitely, what is the nature of the transport equation satisfied by this probability? The answer to this question allows one to study the way in which the statistical properties of the system vary with time under the influence of the perturbation. (c) Does the solution of this transport equation for large times become time-independent in such a way that it corresponds to the expected asymptotic establishment of micro-canonical equilibrium?

An outstanding contribution to the study of these problems is the recent work of van Hove (37 to 40) who also developed a theory of the field-theoretic perturbations in two earlier papers (41). Van Hove recognized, since the perfurbation energy λV extends over the whole system, that it is implied that there exist in the limit—as $N \to \infty$, $v \to \infty$, N/v finite—certain characteristic analytical properties of the matrix elements of λV in the representation corresponding to the unperturbed stationary states of the system— the so-called "diagonal singularity conditions" (D.S.C.). A special form of perturbation theory (41) is used that permits a number of partial summations to be carried out in closed form. Van Hove (38) succeeded in describing by quantum statistics the approach to equilibrium of those systems for which the D.S.C. can be verified.

What are then the D.S.C.? Before we answer this question we must first characterize the Hamiltonian of our system and the basic representation to be used. The unperturbed Hamiltonian H is assumed to give an essentially complete separation of variables. In the limit of a very large system van Hove may assume the occurrence of continuous quantum numbers and unperturbed energies corresponding to the unperturbed Hamiltonian and he leaves out of consideration all discrete quantum numbers such as polarization or spin indices. Thus, in the limit, H is assumed to have a complete set of

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[3] In general, one cannot expect all states to be dissipative, e.g., the ground-state should be non-dissipative. Furthermore the existence of phenomena such as superfluidity or super-conductivity suggests that sometimes very low lying excited states behave nondissipatively.

eigenstates $|\alpha\rangle$ to which correspond eigenvalues $\epsilon(\alpha)$, defined by

$$H|\alpha\rangle = \epsilon(\alpha)|\alpha\rangle$$

which is continuous in all the quantum numbers in α. $|\alpha\rangle$ is further normalized so that $\langle\alpha|\alpha'\rangle$ in the limit considered becomes a product of δ functions for all the variables, i.e.,

$$\langle\alpha|\alpha'\rangle = \delta(\alpha - \alpha')$$

The D.S.C., in general terms, consist of three properties which have to be verified for a given system. We paraphrase van Hove in their statement, omitting details which can be found in the original paper.

Property (i): Take the matrix element $\langle\alpha|V|\alpha'\rangle$ for those states α and α' for which it is not identically zero (i.e. for α and α' differing by the few excitations absorbed or emitted by V) and consider it for those states as function of all distinct quantum numbers contained in α and α'. In the limit of a large system this function exhibits a δ-singularity. This singularity expresses overall conservation of momentum (or wave vector). It does not imply a δ-singularity in the difference $\epsilon(\alpha) - \epsilon(\alpha')$.

Property (ii): Take a higher order matrix element of the type $\langle\alpha|VA_1V \cdots A_nV|\alpha'\rangle$ where $A_1, \cdots, A_n$ are diagonal operations in the $|\alpha\rangle$ representation

$$A_j|\alpha\rangle = |\alpha\rangle A_j(\alpha)$$

Assume each eigenvalue $A_j(\alpha)$ a smooth function of all quantum numbers involved in α. Consider this matrix element for those states α, α' for which it is not identically zero and regard it as a function of all distinct quantum numbers in α and α'. In the limit of a large system, this function exhibits singularities of δ-type originating from the singularities in $\langle\alpha''|V|\alpha'''\rangle$. In addition to the δ-factor expressing overall conversation of momentum (or wave vector) further δ-singularities may occur. They are caused by the fact that the number of intermediate states over which one has to sum when calculating (for a finite system) the expression

$$\langle\alpha|VA_1V \cdots A_nV|\alpha'\rangle = \sum_{\alpha_1 \cdots \alpha_n} \langle\alpha|V|\alpha_1\rangle A(\alpha_1)\langle\alpha_1|V|\alpha_2\rangle \cdots A(\alpha_n)\langle\alpha_n|V|\alpha'\rangle$$

may be larger by one or more factors N (or v) when α is in a special relation to α' than otherwise. The number of such factors always turns out to be one third of the number of relations between quantum numbers in α and α'. Since each quantum number (being a momentum component of an excitation) varies with steps of order $N^{-1/3}$, one gets precisely a δ-singularity when the limit $N \to \infty$ is taken. Higher singularities are never obtained. Among all δ-singularities which are thus possible, none except one implies the equality of the unperturbed energies of initial and final states, i.e. implies a δ-singularity in the difference $\epsilon(\alpha) - \epsilon(\alpha')$. The only exception is the δ-singularity obtained when the state α and the state α' are identical, i.e. when α and α' have the same number of excitations present and these excitations all have the same quantum numbers. In other words, it is a singularity in $\delta(\alpha - \alpha')$. This particular singularity plays a central role in the dynamics of the system and we split the matrix element $\langle\alpha|VA_1V \cdots A_nV|\alpha'\rangle$ in a term containing it and a rest term

$$\langle\alpha|VA_1V \cdots A_nV|\alpha'\rangle = \delta(\alpha - \alpha')F_1(\alpha) + F_2(\alpha, \alpha')$$

The term $\delta(\alpha - \alpha')F_1(\alpha)$ is called the *diagonal* part of the matrix element, and we

call diagonal part of the operator $VA_1V \cdots A_nV$ the operator $\{VA_1V \cdots A_nV\}_d$ defined by

$$\{VA_1V \cdots A_nV\}_d \, | \, \alpha) = | \, \alpha) F_1(\alpha)$$

The rest term $F_2(\alpha, \alpha')$ has no $\delta(\alpha - \alpha')$-singularity, nor has it any δ-singularity implying $\epsilon(\alpha) = \epsilon(\alpha')$.

Property (iii): All what has just been said on the matrix element $\langle \alpha | \, VA_1V \cdots A_nV | \alpha' \rangle$ holds also for the partial matrix elements $\langle \alpha | \, VA_jVA_{j+1}V \cdots A_kV | \alpha' \rangle$ with $1 \leq j \leq k \leq n$. Since the latter are involved in the calculation of the former, one sees that the δ-singularities present in the latter will have to be taken into account when calculating the former by summation over intermediate states. In this summation (still for a finite system)

$$\langle \alpha | \, VA_1V \cdots A_nV | \alpha' \rangle = \sum_{\alpha_1 \cdots \alpha_n} \langle \alpha | \, V\alpha_1 \rangle A(\alpha_1) \cdots \langle \alpha_n | \, V | \alpha' \rangle$$

the singularities of $\langle \alpha_{j-1} | \, VA_jV \cdots A_kV | \alpha_{k+1} \rangle$ manifest themselves as follows (we assume $i \leq j \leq k \leq n$, $k - j < n-1$ and put $\alpha_0 = \alpha$, $\alpha_{n+1} = \alpha'$): when the state α_{j-1} is taken in some special relation to the state α_{k+1}, the number of intermediate states $a_j, \alpha_{j+1} \cdots \alpha_k$ becomes larger by a power of N compensating exactly the decrease in the number of possible choices of the pair $\alpha_{j-1}, \alpha_{k+1}$. We need not consider all possible situations of that kind. The only important ones for our purpose are those corresponding to the diagonal parts of partial matrices $\langle \alpha_{j-1} VA_jV \cdots A_kV | \alpha_{k+1} \rangle$, i.e. to their $\delta(\alpha_{j-1} - \alpha_{k+1})$ singularities. Their effect in the summation is simply that the partial sum obtained by putting $\alpha_{j-1} = \alpha_{k+1}$ gives even when $N \to \infty$ a contribution of the same order of magnitude as the remaining part of the sum. More generally, non-negligible contributions are obtained by simultaneous consideration of diagonal parts of several submatrices, i.e. from partial summations where several pairs of intermediate states are kept equal

$$\alpha_{j_1-1} = \alpha_{k_1+}, \alpha_{j_2-1} = \alpha_{k_2+1}, \cdots (j_r \leq k_r, r = 1, 2, \cdots)$$

A very important point is now that such a pairing of intermediate states only produces (for $N \to \infty$) a non-negligible contribution when no two pairs are interlocked, i.e. when no relation of the form

$$j_r - 1 < j_s - 1 < k_r + 1 < k_s + 1 \qquad (r, s, = 1, 2, \cdots)$$

holds. This is our property (iii).

By means of the conditions described (38), van Hove was able to discriminate between certain dissipative and nondissipative systems. He considers the effect of the perturbation on an initial ($t = 0$) state ϕ_0 coinciding with an unperturbed stationary state $| \alpha_0 \rangle$. The time variation of this state is given by the solution of the Schrödinger equation which can be written

$$\phi_t = U_t \phi_0; \qquad U_t = \exp\left[-it(H + \lambda V)\right] \qquad \text{(III.3.1)}$$

when units are chosen so that $\hbar = 1$. To discuss the occurrence of dissipation van Hove focuses attention on the probability of finding the state ϕ_t in the initial state ϕ_0. This probability is

$$p_t = | \langle \phi_0 | \phi_t \rangle |^2 = | \langle \phi_0 | U_t | \phi_0 \rangle |^2 \qquad \text{(III.3.2)}$$

For a dissipative system one expects that the characteristics of the initial state are eventually lost in the complicated motion of all the many degrees of freedom, i.e., $p_t \to 0$ as $t \to \infty$. In the case of the field-theoretic perturbations the state ϕ_t should retain the initial state as a nonvanishing component, even after very long times, i.e., $p_t \neq 0$ in the limit as $t \to \infty$.

Since van Hove is working in the limit of an infinite system he chooses ϕ_0, to insure proper normalization, as a limit of a wave packet of very narrow extension $\Delta\alpha$ in the continuum of unperturbed states $|\alpha\rangle$ around the unperturbed stationary state α_0,

$$\phi_0 = (\Delta\alpha)^{-1/2} \int |\alpha\rangle d\alpha \qquad \Delta\alpha \in \alpha_0$$ \hfill (III.3.3)

To calculate the matrix element occurring in III.3.2 he chooses an elegant representation of the operator U_t as a complex contour integral of the resolvent operator,

$$R_l = (H + \lambda V - l)^{-1}, \qquad l \text{ a complex number,} \qquad \text{(III.3.4)}$$

viz.

$$\langle \phi_0 | \phi_t \rangle = \frac{i}{2\pi} \int_C dl e^{-ilt} \langle \phi_0 | R_l | \phi_0 \rangle \qquad \text{(III.3.5)}$$

where the integration is to be extended counterclockwise along a contour encircling a sufficiently large portion of the real axis. By virtue of the D.S.C. he can write the matrix element of the resolvent for any two states α', α as

$$\langle \alpha' | R_l | \alpha \rangle = \delta(\alpha' - \alpha) D_l(\alpha) + \text{regular part} \qquad \text{(III.3.6)}$$

where $D_l(\alpha)$ is the eigenvalue of the diagonal part of R_l for the state $|\alpha\rangle$. By the nature of the wave packet representing the initial state, one is concerned solely with

$$\lim_{\Delta\alpha \to 0} \langle \phi_0 | R_l | \phi_0 \rangle = D_l(\alpha_0). \qquad \text{(III.3.7)}$$

Thus, in the absence of a pole in $D_l(\alpha_0)$, one finds by virtue of III.3.2, III.3.5, and III.3.7. that

$$p_t = \lim_{\Delta\alpha \to 0} |\langle \phi_0 | \phi_t \rangle|^2 = \frac{1}{4\pi^2} \left| \int_C dl e^{-ilt} D_l(\alpha_0) \right|^2 \qquad \text{(III.3.8)}$$

Since the integral must vanish as $|t| \to \infty$ (no time's arrow!) one obtains van Hove's characterization of a dissipative system (one subject to statistical mechanical perturbations) by the absence of poles in $D_l(\alpha_0)$. The presence of (simple) poles of $D_l(\alpha_0)$ at $l = E_n$ on the other hand leads to the following expression

$$p_t = \left| \sum_N e^{-iE_n t} \left[\frac{\partial D_l^{-1}}{\partial l}(\alpha_0) \right]_{l=E_n} + \frac{i}{2\pi} \int_{-\infty}^{\infty} dE e^{-iEt} [D_{E-io}(\alpha_0) - D_{E+io}(\alpha_0)] \right|^2 \quad \text{(III.3.9)}$$

where the integral extends over the intervals of the real axis where $D_l(\alpha_0)$ has a finite discontinuity for l crossing the axis. Thus p_t does not vanish

even in the limit as $t \to \infty$. This corresponds to nondissipative perturbed motion.

The importance of the diagonal transitions in determining the gross behavior of large quantum systems subject to the D.S.C. is further illustrated by van Hove's investigation (38) of the probabilities $P(t|\alpha, \alpha_o)$ of transitions in the time interval t between groups of unperturbed stationary states to general order in λ. Before stating the results of this study we must define these transition probabilities. Consider the more general form of the initial state ϕ_o; corresponding to the initial application of the random phase approximation expressing an ignorance of the dynamical details of the initial state,

$$\phi_o = \int |\alpha\rangle c(\alpha) d\alpha \qquad \text{(III.3.10)}$$

where the amplitudes $c(\alpha)$ are incoherently distributed. Further, let A be a diagonal operator (i.e., an operator diagonal in the $|\alpha\rangle$ representation).

$$A|\alpha\rangle = A(\alpha)|\alpha\rangle \qquad \text{(III.3.11)}$$

then the probabilities, $P(t|\alpha, \alpha_o)$, are defined by the relation satisfied by the average

$$\langle \phi_t | A | \phi_t \rangle = \int A(\alpha) d\alpha P(t|\alpha, \alpha_0) d\alpha_o |c(\alpha_o)|^2 \qquad \text{(III.3.12)}$$

where ϕ_t is again given by III.3.1.

By again representing U_t as a contour integral over the resolvent, using the D.S.C. to exploit most fully certain resulting properties of the resolvent operator (41), van Hove derived a non-homogeneous integro-differential equation, the master equation to general order in λ, *not* for $P(t|\alpha, \alpha_o)$, but for $P_E(t|\alpha, \alpha_o)$ related as follows:

$$P(t|\alpha, \alpha_o) = \int_{-\infty}^{\infty} dE P_E(t|\alpha, \alpha_o), \qquad \text{(III.3.13)}$$

where $t \neq o$. The master equation is

$$\frac{dP_E}{dt}(t|\alpha, \alpha_o) = \delta(\alpha - \alpha_o) f_E(t|\alpha) + 2\pi\lambda^2 \int_o^t dt' \int w_E(t - t'|\alpha, \alpha') d\alpha' P_E(t'|\alpha, \alpha') \qquad \text{(III.3.14)}$$

$$- 2\pi\lambda^2 \int_o^t dt' \int d\alpha' w_E(t - t'|\alpha', \alpha) P_E(t'|\alpha, \alpha_o),$$

with the initial condition that

$$P_E(0|\alpha, \alpha_o) = 0$$

The right hand side of III.3.14 differs from the lowest order master equation (Section II.5) by the presence of the inhomogeneous term f_E and the extra time integration, in the other two terms, over the previous evolution of the system. It is the latter feature which is responsible for the non-markovian nature of the process described by this equation, and is to be understood as

as resulting from interference effects between various waves produced by the perturbation. These interference effects are indicative of definite phase relationships whose effects are negligible only in the lowest order of description. The inhomogeneity f_E similarly is a manifestation of the coherent phase relations present in the wave function ϕ_t at all times $t \neq 0$.

The functions $f_E(t/\alpha)$ and $w_E(t|\alpha', \alpha)$ are precisely defined by van Hove (38). In general w_E possesses only formal significance since in order to calculate it to general order one must find the eigenvalues of an irreducible diagonal part of an infinite operator series in λ. The physical significance of w_E arises in that its time integral over the previous history of the system gives the generalized transition ratio. The properties of the functions f_E and w_E which concern us here are: (a) that these functions like P_E are real for all values of their arguments, and (b) the characteristic time dependence of their integrals over α'. The latter is such that (at least for small perturbations) one is led to recognize naturally the existence of two time scales in the limit as $\lambda \to 0$. First there exists a time T_o which does not change as $\lambda \to 0$ for which the inhomogeneous term f_E in III.3.14 is present and completely dominates the homogeneous terms, whose contribution is smaller by a factor λ^2. On the other hand, for dissipative systems a second characteristic time T_1 exists whose magnitude is of the order of $\lambda^{-2}w^{-1}$, where the energy gives the order of magnitude of the transition rate W_o of the zeroth order master equation, such that for times $|t| > T$ and of the order of T_1 the contribution of the inhomogeneous term in III.3.14 is negligible. For such times the temporal behavior of P_E is completely determined by the slow variation of the homogeneous terms. It is precisely this property of III.3.14 that allows van Hove to show that in the limit, as $\lambda \to 0$, $t \to \infty$ in such a way that $\lambda^2 t$ is finite, Equation III.3.14 reduces to the usual zeroth order master equation (Pauli equation) for $P(t|\alpha, \alpha_o)$, except that the transition rates are given correctly to first order in λ rather than only to zeroth order in λ. Thus, van Hove again obtains a demonstration of the Pauli equation in the limit of vanishing λ without repeated use of the random phase assumption, as before achieved (37).

The last portion of reference (38) and the subsequent paper (40) are devoted to the proof that the long time behavior of the solutions of III.3.14 corresponds (for dissipative systems) to establishment of microcanonical equilibrium, the latter being taken for the total Hamiltonian, perturbation included. The main result of this development is as follows: consider a system which in its basic representation of the eigenstates $|\alpha\rangle$ of H (H describing non-interacting plane wave excitations) satisfies the D.S.C. and whose initial state satisfies III.3.10. Consider furthermore a class of operators B, including all operators diagonal in the $|\alpha\rangle$ representation as well as all those non-diagonal operators (the $|\alpha\rangle$ representation) given by convergent series, each term of which is a product of creation and destruction operators for individual plane wave excitations. Then the expectation value of B,

$$\langle B_t \rangle = \langle \phi_o | U_{-t} B U_t | \phi_o \rangle \qquad (\text{III}.3.15)$$

tends, as $|t| \to \infty$, to the microcanonical equilibrium value.

The work of van Hove has stimulated other workers in the field; for example, the work by Brout & Prigogine (42). In general critique of the work of van Hove we make the three points following. (a) The convergence of the perturbation scheme is assumed. As with other perturbation methods in quantum mechanics we shall, in what follows, accept the convergence on faith. (b) Since the D.S.C. have a dominant role in these considerations their representation and validity are important. Clearly, the $|\alpha\rangle$ representation is not intrinsic to the many particle systems considered. As long as investigation is restricted to small perturbations, this particular representation can be supported by the fact that the $|\alpha\rangle$'s are the eigenstates of the Hamiltonian in the limit as $\lambda = 0$. The special significance of the $|\alpha\rangle$ representation for the many particle systems lies in their relation to the physical quantities of principal interest in irreversible processes. These quantities usually have a simple mathematical expression in terms of one-particle operators and these operators, both in crystals as well as gases, have simple matrix elements in the $|\alpha\rangle$ representation; which representation, for systems in which the D.S.C. can be verified, provides a natural way to characterize those very significant B operators whose expectation values trend to the equilibrium micro-canonical expectation values for long time (38, appendix). Indeed, this is typical of cases arising in solid state transport theory, Brownian-motion type problems, weak interactions in gases, etc., where the choice of the $|\alpha\rangle$ representation is obvious, and in which the D.S.C. can be easily verified. In these instances one merely expresses V in terms of the emission and absorption operators of the most obvious free excitations (e.g., phonons or Bloch electrons in solids, free particles in gases, etc.). This need not be the case. Indeed, it has been pointed out by Prigogine & Balescu (43) in connection with their description of irreversible processes in gases that their natural representation of the D.S.C. leads to a contribution of a most important class of all nondiagonal transitions (those corresponding to disconnected diagrams) which is much larger than that of the diagonal transitions. Thus they deny the general validity of a completely general statistical mechanical transport theory based on the diagonal transitions alone, except in what they term a certain number of simple situations. Whether a suitable $|\alpha\rangle$ representation can be found in which the D.S.C. can be verified in a complicated system, as a liquid undergoing transport, remains an open question. (c) The physical interpretation of the entity $P_E(t|\alpha, \alpha_o)$ which satisfies III.3.14 is of importance. Van Hove points out that P_E expresses how much of the transition probability P is contributed by the total energy shell $H + \lambda V = E$. This interpretation presumably is justified in his work (38). Of course, in the limit of weak perturbations ($\lambda \to 0$) the relation of P_E to the total energy shell is confirmed, since in that limit

$$P_E(t|\alpha, \alpha_o) = \delta[\epsilon(\alpha) - E]P(t|\alpha, \alpha_o) \qquad \text{(III.3.16)}$$

A more meaningful interpretation of P_E for finite λ would be helpful.

The irreversible approach toward equilibrium in isolated, so called, "weakly coupled" classical systems has been studied by Brout & Prigogine (42), Prigogine & Balescu (44), and Prigogine & Henin (45), in which special attention is devoted to the diagonal transitions (i.e., the classical counterpart of the D.S.C. of van Hove). The Hamiltonian of the classical weakly coupled systems consists of an unperturbed Hamiltonian which is a sum of N individual contributions $H = \Sigma_i H_i$, i.e., corresponds to a multiply periodic system with N analytic invariants of the motion, and a perturbation energy which couples together these components, λV. The perturbation energy is assumed to be so small that it does not appear in the equilibrium properties of the system, however, it does play a decisive role in the approach of the system to thermodynamical equilibrium since it must be sufficient to destroy the N invariants of the motion.[4] Action $(J_i; i = 1, \cdots, N)$ and angle (α_i) variables are now introduced and an appropriate density in the phase space of these variables is defined $f^{(N)}(J_i \cdots J_N, \alpha_1 \cdots \alpha_N; t)$. This is a solution of the Liouville equation which reduces at time $t = 0$ to a solution for the unperturbed Hamiltonian. The density $f^{(N)}$ and the perturbation potential V then are expanded in the eigenfunctions of the unperturbed Hamiltonian, $\exp[i\Sigma_k n_k \alpha_k]$, n_k integers,

$$f^{(N)}(J_1, \cdots \alpha_N; t) = \sum_{\{n\}} f_{\{n\}}{}^{(N)}(J_1, \cdots J_N; t) \exp\left\{i\sum{}' n_k(\alpha_k - \omega_k t)\right\}$$
$$\text{(III.3.17}$$

$$V = \sum_{\{n\}} V_{\{n\}}(J) \exp\left\{i\sum n_k \alpha_k\right\} \qquad \text{(III.3.18)}$$

where the $\omega_k = 2\pi\nu_k$; ν_k being the characteristic frequencies, $\{n\}$ represents any set of integers $n_1, n_2, \cdots, n_N$, and the $V_{\{n\}}$ are known functions of the J's. The time dependent coefficients $f_{\{n\}}{}^{(N)}$ satisfy in general a complex system of equations obtained by substituting back Equations III.3.17 and III.3.18 into the Liouville equation.

Considering again the limit of an infinite system, the classical analog of the D.S.C. is found in the fact—which has to be verified for the system under consideration—that the diagonal elements of

$$\sum_{\{n''\}} V_{\{n-n''\}} V_{\{n''-n'\}} = V_{\{n-n'\}} \qquad \text{(III.3.19)}$$

which correspond to $\{n\} = \{n'\}$ are at least by a factor N larger than the non-diagonal elements of V^2. If this is the case, and if furthermore the Poincaré resonance condition[5] is satisfied (i.e., the perturbation is essentially

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[4] Moreover it must be impossible to define new invariants which, for $\lambda \to 0$, would reduce to the old invariants.

[5] This states that for every degree of freedom it must be possible to find non-vanishing integers $m, \cdots, m_N$ such that the resonance condition $\Sigma m_k \nu_k = 0$ is satisfied with the Fourier coefficient $V_{m_1 \cdots m_N} \neq 0$.

dissipative), then the classical perturbation theory reduces in the limit, as $\lambda \to 0$, $t \to \infty$, with $\lambda^2 t$ finite, to the diagonal generalized Fokker Planck type equations

$$\frac{\partial f_{\{n\}}^{(N)}}{\partial t} = \lambda^2 \Omega_{\{n\}} f_{\{n\}}^{(N)} \tag{III.3.20}$$

for the $f_{\{n\}}^{(N)}$ with $\Omega_{\{n\}}$ a second order differential operator. It can further be shown that III.3.20 suffices to obtain the usual dissipative approach to thermodynamic equilibrium. In particular if the $f_{\{n\}}^{(N)}$ are initially factorized into a product as shown below

$$f_{\{n\}}^{(N)}(J_1, \cdots J_N; 0) = \prod_{i=1}^{N} \phi_i(J_i, 0) \tag{III.3.21}$$

then the ϕ_i can be shown to satisfy a Boltzmann equation corresponding to weakly coupled systems.

From the nature of the underlying assumptions and the form of the final results (i.e., III.3.20) it appears very likely that this theory is in some sense a classical analog of van Hove's (37). This surmise is considerably strengthened by a demonstration by Brout (46) that III.3.20 is indeed the limit of the lowest order quantum master equation derived by van Hove as $\hbar \to 0$.

The further work by Prigogine and his collaborators on the diagram method, in which the diagonal transitions play but a minor role, is reviewed very briefly in Section IV.3.

III. 4. RELATIONSHIPS BETWEEN GENERAL THEORIES

The explicit relationships between the various formulations of transport theory that have been discussed are physically clear but formally obscure. In only one case has a mathematical analogy been carried through. Rice has considered the question of the equivalence of the condition of diagonal singularity (47) and time smoothing or more general coarse graining in the Kirkwoodian sense.

Write Liouville's equation in the form

$$\mathcal{L}^{(N)} f^{(N)} = i \frac{\partial f^{(N)}}{\partial t} \tag{III.4.1}$$

which has the solution

$$f^{(N)} = \sum_k c_k e^{-i\lambda_k t} \phi_k$$
$$\mathcal{L}^{(N)} \phi_k = \lambda_k \phi_k \tag{III.4.2}$$

where all the λ_k are real, $f^{(N)}$ is the N-body distribution function and the c_k are weighting coefficients. Following van Hove (37) and Brout & Prigogine (42), we divide the Hamiltonian of the system into a perturbation and an unperturbed part, and use angle action variables. The distribution function is then spectrally decomposed in terms of the basis functions of the un-

perturbed Hamiltonian. Considering the interaction energy as a perturbation, the Fourier coefficients of the fine grained distribution function may be shown to change with time as

$$\frac{\partial f_{\{n\}}^{(N)}}{\partial t} = \sum_{\{n'\}} \langle \{n_i\} \mid \exp\left(i \sum n_i \nu_i t\right) \delta\mathcal{L} \exp\left(-i \sum n_i \nu_i t\right) \mid \{n'_i\} \rangle f_{\{n'\}}^{(N)} \langle \{n_i\} \mid \delta\mathcal{L} \mid \{n'_i\} \rangle$$

$$= \frac{1}{(2\pi)^N} \int \exp\left(-i \sum n_i \alpha_i\right) \delta\mathcal{L} \exp\left(i \sum n_i \alpha_i\right) d\alpha_1 \cdots d\alpha_N$$

$$\delta\mathcal{L} = -i \sum \left[\frac{\partial H_{int}}{\partial J_i} \frac{\partial}{\partial \alpha_i} - \frac{\partial H_{int}}{\partial \alpha_i} \frac{\partial}{\partial J_i}\right] \tag{III.4.3}$$

$$\phi_{\{n\}} = \frac{1}{(2\pi)^{N/2}} \exp\left(i \sum n_i \alpha_i\right)$$

$$\lambda_{\{n\}} = -\sum n_i \frac{\partial H}{\partial J_i} = -\sum n_i \nu_i(J)$$

Consider now a coarse graining in angle action space corresponding to the more usual coarse graining in space and time. We immediately find that all expansion coefficients corresponding to space (angle) intervals less than the interval of coarse graining give no contribution to the distribution function. Similarly, coarse graining in time removes all frequencies $\nu_i > \tau^{-1}$. In the perturbation expansion used by Prigogine and Brout, off-diagonal elements correspond to $\{n\} \neq \{n'\}$ and it is just these elements that oscillate most rapidly; the further from the diagonal, the more rapid the oscillation. But the condition of diagonal singularity neglects all terms wherein $\{n\} \neq \{n'\}$ which is equivalent to coarse graining over a very long interval. Coarse graining over a small interval leaves some elements near the diagonal, a result to be desired if transport is not to depend totally on the properties of the entire medium in a nonlocal manner. If the interval of coarse graining is long compared to the basic dynamical event, the diagonal terms make the dominant contribution, and

$$\frac{\partial \bar{f}_{\{0\}}^{(N)}}{\delta t} = \Omega \bar{f}_{\{0\}}^{(N)}$$

$$\Omega = \pi\lambda^2 \sum_{\{n\}}' \sum_{k,k'} n_k n_{k'} \left[\frac{\partial |V_{\{n\}}|^2}{\partial J_k} + |V_{\{n\}}|^2 \frac{\partial}{\partial J_k}\right] \frac{\partial}{\partial J_{k'}} \tag{III.4.4}$$

the superscript ($\sim$) indicating time and phase space smoothing. We therefore suggest that the techniques introduced by Kirkwood (49) and van Hove are closely related. The philosophy espoused in the coarse graining mechanism is in some senses only slightly different from the "objective" criterion sought by Prigogine. The general view to be taken is that irreversibility is generated by the lack or loss of information about the system under study. The explicit coarse graining of a fine grained distribution function, or the projection of a joint probability distribution of two systems onto the subspace of one of them, or the explicit neglect of coherences between the phases of particles

which latter is the physical essence of the diagonal singularity condition, all lead to irreversible behavior. Each of these methods corresponds to a loss of information about the system. It is possible to relate the process of information loss to measurements by noting that in general, there is a limit to resolution posed either by the instrument or the interval between measurements. This is in part the situation envisaged by Kirkwood. If we further note that in the theory of Fourier series it is shown that when a given function is sampled only at intervals Δx, then the maximum frequency that can appear in the Fourier series representation of the function is of order of magnitude $(\Delta x)^{-1}$, and the connection between instrumental coarse graining and rejection of high-frequency components of the distribution function is made clearer.

IV. GASES

IV.1. The Boltzmann Equation

There have been numerous attempts to derive the Boltzmann equation from the first principles of statistical mechanics with the aid of some auxiliary nonmechanical assumptions that relate to the irreversibility. The assumptions required to effect a derivation are basically three in number: the truncation of interactions of higher order than binary collisions, the condition of molecular chaos, and the slow secular variation of $f^{(1)}$ in space. Of these considerations, the molecular chaos is responsible for the irreversibility. Questions of the propagation of chaos are admirably discussed by Grad (50) and herein we only consider how this concept enters a deduction of the Boltzmann equation from first principles.

The starting point of the argument is conveniently taken as the Liouville equation, II.4.1, and its contraction to give the rate of change of the singlet distribution function, II.1.6. Equation III.1.6 is conveniently rewritten (51) in the form

$$\frac{\partial \bar{f}^{(1)}}{\partial t} + \frac{p_1}{m} \cdot \nabla_R \cdot \bar{f}^{(1)} + \mathbf{X}_1 \cdot \nabla_{P_1} \bar{f}^{(1)}$$

$$= -\frac{(N-1)}{\tau} \int_0^\tau \int F_{12} \cdot \nabla_{p_1} K^{(2,2)}(s) f^{(2)}(t) dR_2 dp_2 ds dR_1{}' dR_2{}' dp_1{}' dp_2{}' \tag{IV.1.1}$$

where the pair space transformation function is defined by

$$K^{(n,n)}(rp/r'p'; s) = \int K^{(N,N)}(rpQP/r'p'Q'P'; s) f^{(n/N-n)}(r'p'/Q'P'; t) dP dQ dP' dQ' \tag{IV.1.2}$$

$$f^{(n)}(r, p; t+s) = \int K^{(n,n)}(rp/r'p'; s) f^{(n)}(r'p'; t) dr' dp'$$

with $f^{(n/N-n)}$ the relative probability density of finding the subset n with specified coordinates and momenta. In a similar manner, the Liouville equation for $K^{(N,N)}$ can be contracted to yield

$$\frac{\partial K^{(2,2)}}{\partial s} + \frac{p_1}{m} \cdot \nabla_{R_1} K^{(2,2)} + \frac{p_2}{m} \cdot \nabla_{R_2} K^{(2,2)} + (X_1 + F_{12}) \cdot \nabla_{P_1} K^{(2,2)} + (X_2 + F_{21}) \cdot \nabla_{P_2} K^{(2,2)}$$

$$\text{(IV.1.4)}$$

$$= - \sum \int [F_{1j} \cdot \nabla_{P_1} + F_{2j} \cdot \nabla_{P_2}] K^{(N,N)}(s) f^{(2/N-2)} dP dQ dP' dQ'$$

In the low density limit, when ternary and higher order collisions are neglected, simultaneously three body forces vanish and the right hand side of Equation IV.1.4 becomes identically zero. Equation IV.1.4 is then a Liouville equation in pair space with the solution

$$K_0^{(2,2)} = \delta(R_1 - R_1' - \Delta R_1)\delta(R_2 - R_2' - \Delta R_2)\delta(p_1 - p_1' - \Delta p_1)\delta(p_2 - p_2' - \Delta p_2 \quad \text{(IV.1.5)}$$

with the increments in coordinates and momenta to be calculated from the dynamics of the binary encounter. To utilize this result for the transition probability, Equation IV.1.1 is rewritten with the aid of III.1.11,

$$\frac{\partial \bar{f}^{(1)}}{\partial t} + \frac{p_1}{m} \cdot \nabla_{R_1} \bar{f}^{(1)} + X_1 \cdot \nabla_{P_1} \bar{f}^{(1)} = (N-1) \left[\Omega + \frac{\Theta}{\tau} \right]$$

$$\Omega = -\frac{1}{\tau} \int_0^\tau \int F_{12} \cdot \nabla_{P_1} K_0^{(2,2)}(s) f^{(1)}(t) f^{(1)}(t) dR_2 dp_2 ds dR_1' dR_2' dp_1' dp_2' \quad \text{(IV.1.6)}$$

$$\Theta = \int_0^\tau \int F_{12} \cdot \nabla_{P_1} K_0^{(2,2)}(s) [1 - g^{(2)}(t)] f^{(1)}(t) f^{(1)}(t) dR_2 dp_2 ds dR_1' dR_2' dp_1' dp_2$$

By substitution, the integral term Ω is easily evaluated and found to be

$$\Omega = \int \frac{p_{12}}{\mu} [f^{(1)}(R_1 p_1 - \Delta p_1; t) f^{(1)}(R_1, p_2 - \Delta p_2; t)$$
$$\quad \text{(IV.1.7)}$$
$$- f^{(1)}(R_1 p_1; t) f^{(1)}(R_1 p_2; t)] b \, db \, d\epsilon \, dp_2$$

with p_{12}/μ the relative velocity of the pair, b the collision parameter and ϵ the azimuthal angle specifying the collision. If the distribution functions $f^{(1)}$, and therefore the macroscopic properties of the system, vary only slowly in space, then the term of $O(\Delta R(\tau))$ is easily shown to be negligible relative to the term in Ω explicitly displayed. Note that this approximation is equivalent to discarding the co-volume of the molecules and is responsible for the equation of state derived from the diagonal elements of the pressure tensor being that of an ideal gas, rather than that of a real gas with the second virial coefficient. Thus far we have employed the conditions of slow variation and low density. To discuss the irreversibility requires consideration of the assumption of molecular chaos. In the formulation presented this appears in the condition that the correlation integral Θ be finite at a given initial time. It can then be shown that if Θ is finite at one time, it will remain finite for all time. Thus, the contribution of Θ can be made very small if τ is taken sufficiently large. The combination of Equations IV.1.7 and IV.1.6, followed by a second time smoothing, immediately gives the usual Boltzmann equation.

Before analyzing the derivation given it is pertinent to remark that similar considerations suffice to obtain the Boltzmann equation in quantum

theory, at least in the Born approximation to the scattering problem (52). In the quantum mechanical case, $f^{(N)}$ is replaced by the corresponding Wigner function defined as the Fourier transform of the density matrix. As in the preceding, the phase space transformation function serves as the Green's function explicitly defining the manner in which a pulse propagates. Other than involving details peculiar to quantum mechanics rather than classical mechanics, the philosophy of the calculation is the same as already described and the basic assumptions utilized are also the same.

Consider now the three basic assumptions upon which the argument presented above is based. The restriction that the singlet distribution function vary slowly in space is very mild. Even under the extreme conditions in a shock front it may be a useful approximation, and under ordinary circumstances it is certainly valid to the same extent that local parameters such as temperature, pressure, etc. can be employed as useful variables. The binary collision approximation is also valid in the limit of low densities, and we therefore focus attention on the question of molecular chaos and the related time smoothing.

At least part of the difficulty in analyzing the chaos property arises from the intuitive nature of this assumption. That is, the usual mental image of the gaseous collision process leads to the expectation that chaos will be produced even if absent initially, though this may require many collisions to accomplish. However, if such chaos requires a time interval corresponding to many collision times, then it does not lead to the Boltzmann equation as deduced above. For, in IV.1.7 the relevant time interval is long compared to the duration of a collision but short compared to the mean time between collisions. The problem separates into two overlapping questions: is the initial distribution "chaotic" and is the chaos property propagated?

Consider first the question of initial chaos. Grad (50) has claimed that the class of functions $\{f_n^{(2)}\}$ which is obtained by integration of the class $\{f^{(N)}\}$ chosen to be consistent with a given singlet function, $f^{(1)}$, converges to the product $f^{(1)}(1)f^{(1)}(2)$ as $n \to \infty$. The argument centers on the symmetry of the distribution function in the arguments, positions, and momenta with the net result that the probability density is peaked in those regions of phase space for which the factorized product condition is valid. Unfortunately the detailed proof of this theorem is unpublished. Certainly the fact that the gas is dilute must be used in the argument since the result cannot be valid in dense media. It is not at all clear how the condition that $f^{(1)}$ be "approximately Maxwellian" enters the demonstration since a logical first order approximation to $f^{(1)}$, even in a dense medium, is to choose the distribution to be locally Maxwellian about the mean fluid velocity with a spread determined by the local temperature. Such a choice in no way implies that the pair correlation function has the value unity.

However, assume that at a given time chaos is established. It is clear that whether chaos will or will not be propagated depends in part on the time scale for which Liouville's equation is solved. Even with an initially fac-

torized distribution, it is certainly true that for time intervals that are short compared to the mean time between collisions, a pair of particles that has just collided will be strongly correlated with one another. It is only by the intercession of further collisions with third and fourth body molecules that this correlation can be destroyed. Whereas at equilibrium $g^{(2)}$ has a correlation range (that is, a volume element within which it differs from unity) only of order of magnitude of the range of intermolecular forces, out of equilibrium the correlation range may be much larger. This is a result of the persistance of the initial state. Briefly stated, as time increases there will be an increasingly large number of initial configurations that result in collision, and thus in a certain sense the correlations grow in time. In the absence of intervening collisions the correlations for a pair of particles are essentially constant over a distance equal to the relative velocity multiplied by the time. We immediately note that the effect of time smoothing is to limit the correlation time to τ, successive intervals of length τ being uncorrelated. If τ is taken as long, relative to the duration of an encounter, but short relative to the time between encounters, then smoothing over an interval τ successfully breaks the correlations between successive collisions. There remains, however, an indirect correlation due to the coupling through third-body molecules. Consider the following collision sequence: molecule one collides with molecule two, molecule two rebounds and collides with molecule three, etc., the trajectories being so constructed that molecules two and three would not have collided at that time except for the prior collision with molecule one. It is clear that for this example molecule one has influenced the collisions between molecules two and three. For geometric reasons, the correlation due to these indirect collision sequences must decrease with increasing distance between molecules one and two. That is, in a homogeneous gas, the probability that no intermediate collisions occur between the indirectly coupled collision of molecules two and three following the collision of molecules one and two is of the approximate from $\exp\left(-\left|R_{12}\right|/\lambda_f\right)$ where λ_f is the mean free path and $\left|R_{12}\right|$ is the relative distance between particles one and two. Therefore, outside a sufficiently large volume element in configuration space, the correlation due to indirect collision paths vanishes. We may now state a more restrictive condition on the time interval used for the second time coarse graining. It must be chosen so as to render the correlations due to indirect collisions negligible. Note that a time interval is equivalent to a linear extension of order $\Delta R(\tau)$. In the dilute gas $\Delta R(\tau)$ ought to be of the order of magnitude of a few mean free paths or less.

We may give an alternative description of the persistence of the effects of the initial distribution in terms analogous to the random phase approximation of quantum mechanics (53). Let the initial configuration be specified by a region of phase space D_0. Then at any time t, the trajectory the system follows must start from within D_0 and end in another volume element, say D. But if the initial distribution is defined macroscopically or in insufficient detail microscopically, there are many points in D_0 corresponding to the un-

certainty in the region of phase space at time t. The dependence of the distribution function on the initial state may be characterized by writing

$$\frac{\int_{D_o} f f_o^{(N)} d D_o}{\int f_o^{(N)} d D_o} = \langle f(D_o, t) \rangle_{D_o} \tag{IV.1.8}$$

where $f_o^{(N)}$ is the distribution of possible initial configurations in D_o. Now define a distribution function

$$
\begin{aligned}
f &= \bar{f}(d_o, t) + \phi_t(d_o, t) \\
f &= \langle f(D_o, t) \rangle_{D_o} + \phi_{D_o}(d_o, D, t)
\end{aligned}
\tag{IV.1.9}
$$

where the superscript bar again means a time average, the variable d_o refers to a specific phase point in D_o, and the functions ϕ_t and ϕ_{D_o} are defined by Equation IV.1.9 as the residuals between the indicated averages. The functions ϕ describe the detailed correlations due to indirect causes. Now, the region D_o is defined either by macroscopic variables or an incomplete set of microscopic variables. Any two trajectories originating in D_o must therefore be taken as uncorrelated from our point of view. We are therefore led to conclude that as a condition of factorizability

$$\int_{D_o} \phi_{D_o}(\boldsymbol{R}\boldsymbol{p}', t; d_o, D_o) \phi_{D_o}(\boldsymbol{R}, \boldsymbol{p}'', t, d_o, D_o) d D_o = 0 \tag{IV.1.10}$$

which leads to

$$\langle \bar{f} \rangle_{D_o} = \overline{\langle f \rangle_{D_o}} \tag{IV.1.11}$$

Since by the definition of the functions ϕ

$$
\begin{aligned}
\int_0^\tau \phi_t(t + s) ds &= 0 \\
\int_{D_o} \phi_{D_o}(\boldsymbol{R}\boldsymbol{p}, t, d_o, D_o) d D_o &= 0
\end{aligned}
\tag{IV.1.12}
$$

and therefore the functions ϕ play the role of high frequency Fourier components removed from the distribution function by smoothing over time or initial configuration. As before it requires some smoothing to insure factorizability. Clearly, space smoothing, time smoothing, and smoothing of initial configurations are closely related, though not identical for all values of the relevant variables.

But aside from questions of how chaos and time smoothing are related in very short time intervals it is pertinent to inquire how much chaos is required for the derivation of the Boltzmann equation, and whether or not chaos propagated when large time intervals are considered.

It has not yet been possible to prove in general that the Boltzmann equation propagates the chaos property although it can be shown to be true for some configurations. These configurations are just those for which

the pair of particles is widely separated and do not collide. The basic idea is that when the particles are not close to one another, $f^{(2)}$ and $f^{(1)}(1)f^{(1)}(2)$ have similar time dependence. The residual difference, $f^{(2)} - f^{(1)}(1)f^{(1)}(2)$, can then be related to the residual differences between products of singlet distribution functions and the corresponding higher distribution functions, $f^{(n)}$. When the particles do not collide, simple rectilinear trajectories are traversed and thereby the two particle residuals are related to the initial values of the n-particle residuals. But if $f^{(n)}$ is initially chaotic, the nth order residuals tend to zero and the time dependence of the two particle residuals also tends to zero. Thus the initial chaos is propagated in that set of configurations in which collisions do not occur. Due to the large correlations in the short time interval immediately following a collision, no general proof of the propagation of chaos has yet been constructed.

On the other hand, Kac (54) has shown that the simplified Master equation

$$\frac{\partial \phi(R, t)}{\partial t} = \frac{\nu}{n} \sum_{1 \le i < j \le n} \frac{1}{2\pi} \int_0^{2\pi} [\phi(A_{ij}(\theta)V, t) - \phi(V, t)] d\theta \qquad (IV.1.13)$$

has the property that an initially factorized distribution function remains factorized for all time. In IV.1.13 the symbol V represents a $3n$ dimensional master velocity vector, A_{ij} describes the rotation of the vector V caused by a collision and ν is a constant related to the transition probability for the event just described. The relevance of this demonstration depends upon a detailed justification of the Master equation on the basis of the Liouville equation. This will be taken up in the next section.

IV. 2. BROUT'S ANALYSIS OF THE MASTER EQUATION

We return now to study the relationship between Equations III.1.9 and III.1.4 by the analysis of Brout (55). For simplicity, attention is restricted to a dilute gas of rigid spheres. It is to be noted that for rigid spheres the right hand side of Equation IV.1.4 vanishes, for a collision between rigid spheres is instantaneous, therefore the probability of simultaneous three-body collisions may be neglected. Equation IV.1.4 thereby becomes a Liouville equation in pair space. To establish a convenient notation, rewrite IV.1.4 in the form

$$\frac{\partial K^{(2,2)}}{\partial s} + Y_{12}K^{(2,2)} = 0$$

$$Y_{12} = \frac{p_1}{m} \cdot \nabla_{R_1} + \frac{p_2}{m} \cdot \nabla_{R_2} + F_{12} \cdot \nabla_{P_1} + F_{21} \cdot \nabla_{P_2} \qquad (IV.2.1)$$

If $K^{(2,2)}(0)$ is the initial value of $K^{(2,2)}(s)$, the formal solution is given by Equation IV.1.5 for short times in which only one binary encounter occurs. For longer time intervals $K^{(2,2)}$ can be obtained from Equation IV.2.1 by an iterative integration with respect to time. The formal representation of the transition probability is

$$K^{(2,2)}(s) = K^{(2,2)}(0) + \frac{1}{2} \int_0^s dt_1 Y_{12} K^{(2,2)}(0)$$

$$+ \frac{1}{4} \sum_{j,k} \int_0^s dt_1 Y_{1j} \int_0^{t_1} dt_2 Y_{k_2} K^{(2,2)}(0) dR_j' dR_j dR_k' dR_k dp_j' dp_j dp_k' dp_k + \cdots \qquad (IV.2.2)$$

The first term in IV.2.2 corresponds to free motion and the second term to the isolated binary encounter with solution given by IV.1.5. In general, in the third and higher terms the phase space integration is over the coordinates and momenta of all "intermediate particles," i.e., all particles which collide with 1 and 2 other than 1 and 2 themselves. Suppose that molecules j and k are distinct. Then in the third term, Y_{ij} operates on $K^{(2,2)}(0)$ just as for zeroth order, except that the integrand contains the factor t_1. Performing the indicated integrations leads to a product of two terms, each of the same structure as the second term in IV.3.2. When the indices j and k are the same, molecule j is involved in two successive collisions but the result of the operations is the same as above. If $k=1$, $j=2$, the pair of molecules recollides after the initial encounter. In an infinitely extended dilute system the recollisions of a given pair of molecules may be neglected. With the notation T for the integral operator, repetition of the arguments just given for the nth order contribution leads to

$$K^{(2,2)}(s) = \sum_{n=0}^{\infty} \frac{s^n}{n!} T^n K^{(2,2)}(0)$$

$$\frac{\partial K^{(2,2)}}{\partial s} = T K^{(2,2)}(s) \qquad (IV.2.3)$$

To obtain Equation IV.2.3 recollision terms and closed cycles of collisions such as described by the sequences, (ij) (ik) (ij) are neglected. It is this omission that leads to the elimination of Poincaré cycles since the collision cycles obviously tend to reconstruct or repeat an initial configuration in some sense. Since the vast majority of terms do not correspond to closed cycles, there is probably little error in this neglect when the system contains many molecules and is dilute. Strictly speaking the neglect is only valid (if at all) in the limit of infinite systems.

Equation IV.2.3 may be formally represented as an ordered exponential, the time irreversible trajectory being characteristic of a Master equation describing a Poisson process. The formal equation represents a succession of disjoint events with the molecules traveling as free particles between collisions. Of course the asymptotic dependence of $K^{(2,2)}$ on the time variable depends upon the correlation between the disjoint events, and this remains true for the contracted transition probability $K^{(1)}(s)$. The function $K^{(1)}(s)$ is immediately obtained from $K^{(2,2)}$ by integration over the coordinates and momenta of the initial and final states of the second particle of the pair of particles.

The connection of IV.2.3 and IV.1.4 can be obtained from a consideration

of the probability distribution of path lengths of a single molecule between collisions. If the path length is ΔR_i this is

$$p(\Delta R_i)d\Delta R_i = \frac{d\Delta R_i}{\lambda_f(c)} \exp\left\{-\Delta R_i/\lambda_f(c)\right\} \tag{IV.2.4}$$

where the mean free path $\lambda_f(c)$ may vary with the speed c. It may readily be shown (56) that the diffusion coefficient is related to the path taken by

$$\left.\begin{aligned}
\mathfrak{D} &= \frac{1}{3} \int \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-mc^2/2kT\right\} 4\pi c^2 \psi(c) dc \\
\psi(c) &= \lambda_f(c) + \int G(c, c')\psi(c')dc' \\
G(c, c') &= \int K^{(1,1)}(Rp/R'p'; s)RdR'dR
\end{aligned}\right\} \tag{IV.2.5}$$

and thus the singlet transition probability is again related to the diffusion coefficient, albeit the form of the relation appears different.

The correlation in flights of a single molecule is related to the chaos problem discussed previously in the sense that Equation IV.2.5 is established for the case of many flights. If a molecule with velocity c suffers a series of collisions it can be shown that after n collisions, each of the moments of the final velocity forgets at least as fast as $(\frac{1}{2})^n$. Five collisions are needed to attain correlation coefficients as small as 0.03. However, the assumption of chaos used to factorize the distribution function in the kernel of the Boltzmann equation introduces a one-sided forgetfulness before the collision. Thus the assumption of chaos in the Boltzmann equation is in the ensemble sense equivalent to following a single particle over many free flights interrupted by collisions. The single particle transition probabilities are accordingly the same in the limit of large time intervals.

IV.3. PRIGOGINE'S ANALYSIS OF IRREVERSIBLE PROCESS IN GASES

Prigogine & Balescu (43) have developed an elegant and incisive analysis of the approach to equilibrium in gases. The basis of the analysis lies in the Fourier decomposition of the N body distribution function, $f^{(N)}$, and the classification of terms which appear in the decomposition according to powers of t, N/v, and λ, where λ is the coupling constant of the intermolecular potential energy.

Starting from the Hamiltonian

$$H = \sum_j \frac{p_j^2}{2m} + \lambda \sum_{j<n} V_{jn}(|R_j - R_n|) \tag{IV.3.1}$$

and assuming that V_{jn} is expressible in the Fourier series

$$V_{jn} = \frac{1}{v} \sum_l V_l \exp\left\{il\cdot(R_j - R_n)\right\} \tag{IV.3.2}$$

where V_l depends only on the absolute value of l for the case of central forces, the Liouville equation becomes

$$\frac{1}{v^r} \frac{\partial}{\partial t} a_{k_\alpha \cdots k_r}^{\alpha \cdots \nu} = \frac{\lambda}{v} \sum_{m<n} \exp \left\{i \sum_a^\gamma k_j \cdot p_j t\right\} \Big[\langle k_\alpha \cdots k_r | \delta \mathcal{L}_{mn} | 0 \rangle a_o$$

$$+ \frac{1}{v} \sum_j \sum_{k_j}' \langle k_\alpha \cdots k_r | \delta \mathcal{L}_{mn} | k_j' \rangle a_{k_j}{}^j \exp - i k_j' \cdot p_j t \tag{IV.3.3}$$

$$+ \frac{1}{v^2} \sum_{j<s} \sum_{k_j} \sum_{k_s}' \langle k_\alpha \cdots k_r | \delta \mathcal{L}_{mn} | k_1' k_s' \rangle a_{k_j k_s}{}^{js} \exp \left\{ -i(k_j' \cdot p_j + k_s' \cdot p_s) t \right\} + \cdots$$

where $f^{(N)}$ is itself expressed as

$$f^{(N)} = \frac{1}{(8\pi^3 v)^N} \Bigg[a_o + \frac{1}{v} \sum_k' \sum_j a_{kj} \exp \left\{ i k \cdot (R_j - p_j t) \right\}$$

$$+ \frac{1}{v^2} \sum_k' \sum_{\substack{k' \\ k+k' \neq 0}}' \sum_{j<l} a_{pk'}{}^{jl} \exp \left\{ i k \cdot (R_j - p_j t) + i k' \cdot (R_l - p_l t) + \cdots \right\} \Bigg] \tag{IV.3.4}$$

For time-independent Fourier coefficients, a_o, $a_k{}^j$, $\cdots$, Equation IV.3.4 is the solution of the free particle Liouville equation, i.e., when $\lambda = 0$. Equation IV.3.3 is obtained by substitution of IV.3.4 and IV.3.2 in the Liouville equation, integration over coordinates and using the orthogonality properties of $\exp(i k \cdot x)$. The reduced equation relates the rate of change of the Fourier coefficient corresponding to r independent wave vectors being non-zero $a_{k_\alpha \ldots k_r}{}^{\alpha \cdots \nu}$, to the Fourier coefficients of $f^{(N)}$, the expansion being ordered according to the number of nonvanishing wave vectors. Thus a_o is the Fourier coefficient corresponding to zero wave vectors for all molecules, $a_k{}^j$ that corresponding to $k \neq 0$ for molecule j and zero wave vectors for all other molecules, etc. Finally, the matrix element connecting $a_{k_\alpha \ldots k_r}{}^{\alpha \cdots \nu}$ (r indices) with $a_{k_j' \ldots k_s'}{}^{j \cdots s}$ (s indices) is related to the intermolecular potential by

$$\langle k_\alpha \cdots k_r | \delta \mathcal{L}_{mn} | k_j' \cdots k_s' \rangle = \left(\frac{1}{8\pi^3 v}\right)^N \int dR^{(N)} \exp \left\{ -i \sum_a^\gamma k_i \cdot R_i \right\} V_{il} t$$

$$\cdot (\nabla_{p_m} - \nabla_{p_n}) \exp \left\{ i l \cdot (R_m - R_n) \right\} \exp \left\{ i \sum_i^s k_i' \cdot R_i \right\} \tag{IV.3.5}$$

The matrix element is clearly a differential operator acting on the momenta. It is nonvanishing only if m and n are in the set $\{\alpha \cdots \nu, j \cdots s\}$, and may be physically interpreted as representing the transition from $k_j' \cdots k_s' \to k_\alpha \cdots k_r$ due to an interaction between molecules m and n. In this transition all wave vectors except k_n', k_m', remain constant. Due to the invariance of the Hamiltonian with respect to translation the conservation condition

$$k_m' + k_n' = k_m + k_n$$

must be satisfied, a representation of the conservation of momentum.

To evaluate the matrix elements appearing in IV.4.3, Prigogine and Balescu have invented a diagrammatic notation and from the number of vertices and the structure of vertices they deduce the asymptotic dependence

of the matrix element on λ, t, and N/v. It would take us too far afield to reproduce the analysis of the Boltzmann equation by these methods. However, several relevant remarks come to mind. The set of equations obtained by integrating over the momenta of all particles except those of a given set is identical with the Fourier analysis of the reduced set of coupled integral equations derived by Kirkwood, Born and Green, Yvon and Bogolubov. In the case of weak coupling it can be shown that in the first approximation, the distribution function for the momenta, $\phi^{(N)}$ satisfies the relation

$$\frac{\partial \phi^{(N)}}{\partial t} = \frac{\pi \lambda^2}{v} \sum_{j<m} \int dl \,|\, V(l)\,|^2 (\nabla_{pj} - \nabla_{pm}) \delta \left(l \cdot \frac{p_{jm}}{\mu} \right) l \cdot (\nabla_{pj} - \nabla_{pm}) \phi^{(N)} \quad \text{(IV.3.6)}$$

which is the master equation first obtained by Brout and Prigogine. The reduced momentum distribution function is connected to a hierarchy by the dependence of $\phi^{(1)}$ on $\phi^{(2)}$ and so forth. The fundamental difference between this set of coupled equations and the Kirkwood *et al.* hierarchy is that this set is closed in configuration space. To close the hierarchy in momentum space, a natural assumption would be $\phi^{(2)} = \phi^{(1)}(1)\phi^{(1)}(2)$ since this expresses chaos in momentum space. That is, it is anticipated that the momentum correlations die out with increasing inter-particle separation and a non-factorized $\phi^{(2)}$ represents momentum correlations which are independent of distance.

For the case of strong interactions an expansion in powers of the concentration is sought by a reclassification of diagrams. In this case it is found that

$$\frac{\partial f^{(2)}}{\partial t} + \frac{p_{\alpha\beta}}{\mu_{\alpha\beta}} \cdot \nabla_{R\alpha} f^{(2)} - \nabla_{R\alpha} V_{\alpha\beta} \cdot (\nabla_{p\alpha} - \nabla_{p\beta}) f^{(2)}$$

$$= \frac{N}{v} \left[\int dp_j \int d\omega \left\{ \frac{p_{\alpha j}}{\mu_{\alpha j}} \sigma_{\alpha j} [f_f{}^{(2,3)}(R_\alpha R_\beta p_\alpha' p_\beta p_j'; t) - f_f{}^{(2,3)}(R_\alpha R_\beta p_\alpha p_\beta p_j; t)] \right. \right. \quad \text{(IV.3.7)}$$

$$\left. \left. + \text{[same term with } \alpha \text{ and } \beta \text{ interchanged]} \right\} \right]$$

and

$$f_+{}^{(2,3)} = f^{(2,3)} + \nabla R_\alpha \tilde{V}_{\alpha\beta} \cdot (\nabla_{p\alpha} - \nabla_{p\beta}) f^{(2,3)}$$

$$\tilde{V}_{\alpha\beta}(R_\alpha R_\beta p_\alpha p_\beta) = \int_0^\infty d\tau V_{\alpha\beta} \left(\left| R_\alpha - R_\beta - \frac{p_{\alpha\beta}}{\mu_{\alpha\beta}} \tau \right| \right) \quad \text{(IV.3.8)}$$

The distribution function $f^{(2,3)}$ is asymmetric in that it refers to three momenta but only two coordinates. As usual, $\sigma_{\alpha j}$ is the scattering cross section for molecules α and j; and $d\omega$ is an element of solid angle. Note that Equation IV.3.7 involves a time average of the intermolecular pair potential along an unperturbed trajectory of the two particles.

The general technique used to obtain Equations IV.3.6 and IV.3.7 was to sum classes of diagrams ordered in part according to the number of nonvanishing wave vectors. Successively higher approximations are obtained by summing the contributions of terms with successively larger numbers of nonvanishing wave vectors and more complicated sequences of nonvanishing

sets. This procedure of diagram selection and subsequent construction of reduced asymptotic equations constitutes the most elegant discussion of the approach to equilibrium in gaseous systems yet devised. The salient features are clear. First, the asymptotic evaluation of the matrix elements by summing diagrams is only valid for large systems for which $N \to \infty$, $v \to \infty$, but N/v remains constant. Second, the introduction of irreversibility appears in this formalism as a cascade mechanism by which the time dependence of a given Fourier component of the distribution function is related to different order Fourier components (i.e., different numbers of nonvanishing wave vectors). For large system $f^{(N)}$ cannot be reconstructed from a knowledge alone of the Fourier component with all $k = 0$, and therefore $f^{(N)}$ cannot be calculated from the reduced equations for a_2, etc. In general, for large systems a_2 depends upon a_0 but not upon a_3 or a_4, and the change of a_0 is not related to the change of a_3, $a_4 \cdots$. This asymmetry applies only to the low order Fourier components since the calculation of $f^{(N)}$, or an average dependent upon $f^{(N)}$, requires the summation of many diagrams, each individually giving rise to a very small contribution, but in sum giving rise to a finite contribution. Thus a function of all coordinates and momenta does not display irreversibility. In fact, irreversibility is only manifest in the low order Fourier components because the number of diagrams to be summed is small enough that the individual diagrams making infinitesimal many body contributions do not give rise to a finite contribution. This procedure provides a justification for the arguments used in the preceding sections to study the H theorem. Moreover, the argument is related to the relation between coarse graining and the systematic neglect of high order Fourier components of the distribution function, and Mayer's Theorem provides connections between the above analysis and the analysis presented earlier.

V. LIQUIDS

V.I. Hard Sphere Liquids

Perhaps the simplest of all dense fluids is the rigid sphere liquid. In the state of equilibrium, the pair correlation function depends only upon the density, and the equation of state has the simple form

$$\frac{pv}{kT} = 1 + \frac{2\pi\sigma^3}{3v} g_o^{(2)}(\sigma)$$

where σ is a rigid sphere diameter. Because of the impulsive nature of the interactions, simultaneous ternary collisions may be neglected even though successive binary collisions must be considered. Moreover, in the limit of very short time intervals only uncorrelated binary collisions occur. Thus a drastic simplification appears possible, as well as a natural expansion scheme wherein binary collisions, successive pairs of binary collisions, and successive triplets of binary collisions, . . . are taken into account by successive orders of approximation.

It is clear that in the limit of very short time intervals, when only un-correlated binary collisions are considered, an analysis similar to that of Section IV.1 may be used. However, it is no longer permissible to replace the pair distribution function by a product of singlet distribution functions since $g^{(2)}$ is not unity at small distances of approach in a dense medium. In the limit of very small time intervals τ, the rate of change of the distribution function (59) is

$$\lim_{\tau \to +0} \frac{\partial \bar{f}^{(1)}}{\partial t} + \frac{p_1}{m} \cdot \nabla_{R1} \bar{f}^{(1)} = (N-1) \int \left[\bar{f}^{(2)}(R_1, R_1 + \sigma k, p_1 - \Delta p_1, p_2 - \Delta p_2; t) \right.$$
$$\left. - \bar{f}^{(2)}(R_1, R_1 + \sigma k, p_1, p_2; t) \right] \frac{p_{12}}{\mu} \, b \, db \, d\epsilon \, dp_2 \tag{V.1.1}$$

It is important to note that Equation V.1.1 differs from the Enskog modi-fication of the Boltzmann equation in having the pair distribution functions evaluated at the same point before and after collision. This expresses that in the limit $\tau \to +0$, a pair of rigid spheres can instantaneously exchange momentum, but cannot change relative position.

To solve this integro-differential equation the pair correlation function must be specified. If it is assumed that $g^{(2)}$ is independent of momenta and determined by the local density, Equation V.1.1 may be solved by the techniques developed for dilute gases. The results are (60):

$$\eta = \frac{5kT}{8\Omega^{(2,2)}} \left[\frac{1}{Ng_o^{(2)}(\sigma)} + \frac{8\pi\sigma^3}{15v} + \left(\frac{4\pi\sigma^3}{15 \, v} \right)^2 Ng_o^{(2)}(\sigma) \right]$$
$$\kappa = \frac{75k^2T}{32m\Omega^{(2,2)}} \left[\frac{1}{Ng_o^{(2)}} + \frac{14\pi\sigma^3}{15v(\sigma)} + \frac{16}{75} \left(\frac{\pi\sigma^3}{v} \right) Ng_o^{(2)}(\sigma) \right] \tag{V.1.2}$$
$$\Omega^{(2,2)} = \left(\frac{4\pi kT}{m} \right)^{1/2} \sigma^2$$

and differ only slightly from the results obtained by Enskog (61). The vis-cosity is in fact the same and κ differs only by a few per cent in the v^{-1} and v^{-2} terms from that computed in Enskog's theory. Enskog's derivation is based upon geometric arguments and plausible physical considerations. He introduced what is now known as the equilibrium pair correlation function, evaluated the collisional transfer, but maintained all other dilute gas ap-proximations. In other investigations, Collins & Raffel (62), and Longuet-Higgins & Pople (63) have also discussed the theory of transport in a dense fluid of hard spheres. The first of these investigations follows closely the original calculations of Enskog with the modification that the concentration of the centers of the nearest neighbors around a specific collision sphere is assumed to be given by the reciprocal of the molecular free volume instead of the reciprocal of the molecular volume. The second investigation proceeds by physical arguments from the two assumptions that (a) the spatial pair distribution function depends only on the temperature and density and not

on the temperature gradient or rate of strain, and (b) that the velocity distribution function of a single particle is Maxwellian with a mean equal to the local hydrodynamic velocity, and a spread determined by the local temperature. The method used avoids the systematic study of the behavior of the singlet space distribution function and therefore leads to a lower order approximation than that of the Enskog theory. Lastly, Curtiss & Snider (64) have advanced an approach to moderately dense gases in which all the simplifying features of the Maxwell-Boltzmann equation are retained but included are terms derived from the spatial variation of the singlet distribution, and the collisional transfer is evaluated. This addition provides, in the limit of equilibrium, for the contribution of the second virial coefficient in the equation of state. Their work is referred to again in the final discussion.

To analyze the theory it will be recalled that the principal assumptions made in the analysis of Rice *et al.* (59) are:

(a) The evolution in time of a two-body subset is given by the pair Liouville equation for the transformation or distribution function; i.e., the dynamics of the system is determined by binary collisions only, with the exclusion of correlated successive binary, triple, etc. collisions. This hypothesis, essential for dilute gas theory, may be expected to hold at finite densities for the particular model of hard spheres in the limit as the time interval τ appearing in the transformation function approaches an arbitrarily small but positive value. It is clear that the hypothesis does not hold for any molecular model at finite density and finite τ, for then the dynamics would be influenced by higher order collisions. The conjecture that triple collisions, etc., need not be taken into account for hard spheres in a finite fluid requires analytical verification which has not been presented so far (97).

(b) The pair correlation function is taken to be independent of momenta and is approximated by the equilibrium pair correlation function.

(c) With the time scale chosen, the time interval is so short that two molecules exchange momentum at constant intermolecular separation. A complete collision does not require appreciable motion of the centers of mass of the molecules.

The results can be compared with the work of Enskog and Curtiss & Snider. Enskog's modification of the Maxwell-Boltzmann equation, presumed to be valid for a gas of hard spheres at arbitrary density[6] is

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[6] Enskog used the symbol Y for the function which represented the shielding effect on the colliding pair of molecules of all molecules, other than the pair. He proposed that this function be determined from the equation of state and the identification with the equilibrium pair correlation function may be made. At equilibrium the pair correlation function is independent of position in space in the absence of external forces and neglect of surface effects and depends only on the relative configuration of two molecules. Thus, in terms of the equation of state, $(pv/kT) = 1 + (2\pi\sigma^3/3v) Y$ completing the identification of $g_0^{(2)}(\sigma)$ and Y.

$$\frac{\partial \bar{J}^{(1)}}{\partial t} + \frac{p_1}{m} \cdot \nabla_{R_1} \bar{J}^{(1)} = \int \left[Y\left(R_1 + \frac{\sigma k}{2}\right) \bar{J}^{(1)}(R_1, p_1 - \Delta p_1; t) \bar{J}^{(1)}(R_1 + \sigma k, p_2 - \Delta p_2; t) \right.$$

$$\text{(V.1.3)}$$

$$\left. - Y\left(R_1 - \frac{\sigma k}{2}\right) \bar{J}^{(1)}(R_1, p_1; t) \bar{J}^{(1)}(R_1 - \sigma k, p_2; t) \right] \frac{p_{21}}{\mu} \, b db d\epsilon d p_2$$

The Enskog theory of dense gases is based on a perturbation solution of Equation V.1.3 identical in principle with the one used in the theory of dilute gases. The expansion of Equation V.1.3 in a Taylor series about R_1 yields,

$$\frac{\partial \bar{J}^{(1)}}{\partial t} + \frac{p_1}{m} \cdot \nabla_{R_1} \bar{J}^{(1)} = J_1' + J_2' + J_3'$$

$$J_1' = Y \int \left[\bar{J}^{(1)}(R_1, p_1 - \Delta p_1; t) \bar{J}^{(1)}(R_1, p_2 - \Delta p_2; t) - \bar{J}^{(1)}(R_1 p_1; t) \bar{J}^{(1)}(R_1 p_2; t) \right] d\sum$$

$$J_2' = Y \int \left[k \cdot (\bar{J}^{(1)}(R_1, p_1 - \Delta R_1; t)(\nabla_{R_1} \bar{J}^{(1)}(R_1 p_2 - \Delta p_2; t) \right.$$

$$\text{(V.1.4)}$$

$$\left. + \bar{J}^{(1)}(R_1 p_1; t) \nabla_{R_1} \bar{J}^{(1)}(R_1 p_2; t) \right] d\sum$$

$$J_3' = \frac{\sigma}{2} k \cdot \nabla_{R_1} Y \int \left[\bar{J}^{(1)}(R_1 p_1 - \Delta p_1; \bar{f})^{a(1)}(R_1 p_2 - \Delta p_2; t) \right.$$

$$\left. + \bar{J}^{(1)}(R_1 p_1; t) \bar{J}^{(1)}(R_1 p_2; t) \right] d\sum$$

$$d\sum = \frac{p_{12}}{\mu} \, b db d\epsilon d p_2$$

Comparison with the corresponding expansion of Equation V.1.1 shows disagreement in the spatial dependence of the correlation and distribution functions. A source of disparity is evident, for in Enskog's verbal derivation use is made of the phrases "before the collision" and "after the collision" in reference to the independent variables of these functions; in the case of configuration coordinates they are assigned the above values. However, the analysis of Kirkwood *et al.* (59) clearly exhibits the fact that in the limit of small time intervals τ the times referred to in the phrases "before the collision" and "after the collision" becomes identical and therefore the differences between the respective configuration coordinates vanish.

An objection to this argument could be made by claiming that Enskog's transport equation does not depend on the specification of a time interval τ nor on its duration. The claim is not valid: Enskog's transport equation includes only parameters sufficient for the description of binary collisons so that the time evolution of the distribution function as prescribed by his equation is determined solely by a binary collision mechanism. It was seen, however, that the validity of this approximation for the evaluation of the dynamics of the system is appropriate, at finite density, only as the time interval τ approaches zero regardless of the particular analytical model chosen for the interaction between molecules. The limitation on the interval τ, infinitesimally small, is necessary because thus, although successive un-

correlated collisions are included for consideration, correlated binary collisions, triple collisions, etc. are excluded. At moderate densities this may suffice but it becomes untenable at high densities.

In the preceding analysis, a difference has been demonstrated between the equation derived by Rice *et al.* and that derived by Enskog. It is not to be implied that one is necessarily correct and the other incorrect. In fact, a detailed examination reveals that the differences are due to variations in the point at which the hard sphere potential is introduced. In the Rice *et al.* (59) analysis, the computation is carried as far as possible without explicit introduction of the nature of the potential. Thus, in the region where higher order collisions may be neglected, the equations of Section IV.1 are valid for any potential. The hard sphere potential is first used in Equation V.1.1. In contrast, the Enskog treatment introduces the discontinuous potential at the very outset of the calculation. With this choice, the integration of the Liouville equation must be done carefully since $f^{(2)}$ is discontinuous in the region of integration. The fact that two different equations arise when the nature of the potential is discontinuous and the discontinuity is first introduced at two different points is reminiscent of the differences between the Kirkwood and the Born-Green formulations for the calculation of $g_o^{(2)}$ at equilibrium in a liquid. In that case the use of the superposition relation at different points in the analysis leads to two different final equations.

It is a matter of choice as to which equation is to be preferred. The Enskog equation is consistent because the hard sphere potential is used at all times. The Rice *et al.* equation has the advantage that, since no real hard sphere fluids exist, the equation is the logical limit as $n \to \infty$ when the potential is of the form $V = (\sigma/R)^n$. This corresponds to a definite physical picture and classification scheme for fluids.

The transport equation used by Curtiss and Snider was derived by Bogolubov (65) and Born & Green (66):

$$\frac{\partial \bar{f}^{(1)}}{\partial t} + \frac{p_1}{m} \cdot \nabla_{R_1} \bar{f}^{(1)} = \int \bar{f}_o^{(1)}(1) \bar{f}_o^{(1)}(2)[\Phi_{10} + \Phi_{20} - \Phi_1 - \Phi_2] d\sum + J_1'' + J_2''$$

$$J_i'' = \frac{2}{m^2} \int \nabla_R V \cdot \frac{\nabla p_{12}(\Delta_i)}{\mu} dR d p_2$$

$$\Delta_1 = \frac{R'}{2} \cdot [\bar{f}_o^{(1)}(1) \nabla_{R_1} \bar{f}_o^{(1)}(2) - \bar{f}_o^{(1)}(2) \nabla_{R_1} \bar{f}^{(1)}(1)] \qquad (V.1.5)$$

$$\Delta_2 = \frac{R}{2} \cdot \nabla_{R_1} \bar{f}_o^{(1)}(1) \bar{f}_o^{(1)}(2)$$

$$\bar{f}^{(1)}(1) = \bar{f}_o^{(1)}(1)[1 + \Phi_1]$$

The pair correlation function is assumed to be unity, and all density dependent terms are thought to be included which lead, in the equilibrium limit, to the equation of state up to and including the second virial coefficient. Since derivatives with respect to momentum appear in the first

density correction, this transport equation differs from the present one as well as from that of Enskog.

A comparison of the results obtained for the transport coefficients is given in Table V.1.

TABLE V.1

$$\kappa_{\text{(Curtiss \& Snyder)}} = \kappa_0 \left[1 + \frac{29}{90} \frac{\pi\sigma^3}{v} + \cdots \right]$$

$$\kappa_{\text{(Rice et al.)}} = \kappa_0 \left[1 + \frac{31}{65} \frac{\pi\sigma^3}{v} + \cdots \right]$$

$$\kappa_0 = \frac{75k}{64\sigma^2} \left(\frac{kT}{m\pi} \right)^{1/2}$$

$$\eta_{\text{(Curtiss \& Snyder)}} = \eta_0 \left[1 + \frac{7}{30} \frac{\pi\sigma^3}{v} + \cdots \right]$$

$$\eta_{\text{(Rice et al.)}} = \eta_0 \left[1 + \frac{7}{60} \frac{\pi\sigma^3}{v} - \cdots \right]$$

$$\eta_0 = \frac{5}{16\sigma^2} \left(\frac{mkT}{\pi} \right)^{1/2}$$

$$g_0^{(2)}(\sigma) = 1 + \frac{5}{12} \frac{\pi\sigma^3}{v} + 0.1274 \left(\frac{\pi\sigma^3}{v} \right)^2 + \cdots$$

The expression obtained by Curtiss and Snider should agree with the others shown in Table V.1 if $g_0^{(2)}(\sigma)$ is set equal to unity. However, no agreement is obtained, even when $g_0^{(2)}(\sigma)$ is expanded in powers of the density.[7]

It has been indicated several times that the modified Boltzmann equation [Eq. (V.1.1)] is valid in the limit as the time interval, over which the distribution functions are coarse grained, tends to $+0$. Without such a limiting process the interval of time smoothing is sufficiently long so that many successive correlated binary collisions occur during the coarse graining, and no simple equation of the form of Equation V.1.1 is obtainable. It is therefore clear that a modified Boltzmann equation such as Equation V.1.1 describes only part of the flux of momentum and energy; namely, that due to independent binary collisions. Recent comparisons of experiment with the calculated viscosity of the dense rigid sphere fluid show that if the data are made to agree in the low density region, there is a very large deviation at high densities. Moreover, this deviation increases with increasing density. The Tables shown in Chapman and Cowling are fit at the observed minimum of the viscosity-density isotherm and deviate very markedly from the

[7] A private communication has informed the author that the published transport coefficients for hard spheres derived by Curtiss and Snider are in error. (Note added at page proof stage.)

observed low density viscosity. The hard sphere calculations should be best at very high densities where relative molecular motion is highly hindered, with the consequence that only small changes in attractive energy occur over the average possible range of separations of a pair of molecules. Hard spheres are a poorer approximation in the low density region where the molecules are sufficiently far apart to be essentially free except when undergoing collision. In particular, the hard sphere diameter is a function of temperature at low density. The observed deviation at high densities, when the data are fit at low densities, argues that part of the flux of momentum has been neglected.

In Kirkwood's general theory of transport the motion of an individual molecule is analyzed with the aid of analogies from the theory of Brownian motion. In particular, the frictional coefficient, which is related to the intermolecular force, is assumed to have a plateau value and be constant over an interval of time that is neither too short nor too long. This hypothesis has been examined in detail for a Rayleigh gas (67) (dilute heavy particles in a gas of light molecules, with the light gas always maintained at equilibrium) and shown to be in agreement with the deductions from both the Fokker-Planck equation and the hypothesis of the phenomenological theory of Brownian motion (that the distribution of changes of momentum of the heavy particle is normal). For this case at least, the plateau value of the frictional coefficient is rigorously established. Collins and Raffel have calculated from their treatment the frictional coefficient in a dense rigid sphere fluid due to independent binary collisions. Despite the approximations inherent in their model it is likely that their conclusions are basically correct. They find that the frictional coefficient depends strongly upon the particle velocity when the ratio of the mass of the moving molecule to those in the surrounding medium is not large. This result may be due to the successive correlated binary collisions neglected in the analysis, with the consequence that the time interval, over which the frictional coefficient is computed, is, by restriction of the method, too short to be in the plateau region. Of course, the average frictional coefficient (averaged with respect to velocity) shows no such velocity dependence, in agreement with the direct calculation of the self diffusion coefficient from the matter flux (68). It is interesting to note that the machine calculations of Alder and Wainwright indicate that only a very few collisions are necessary for randomization of the velocity of a molecule (in 97). The treatment of successive binary collisions requires the solution of a restricted three-body problem, and is probably worth undertaking in view of the above comments.

Finally, it should be pointed out that the method introduced by Enskog and used by Rice *et al.* to evaluate the perturbation function neglects any possible contribution of the form of a perturbation to the equilibrium pair correlation function times the zero order singlet distribution functions. This neglect cannot be rectified within the framework of the modified Boltzmann

equation used by Rice *et al.* since, in the deduction of this equation, the isotropy of the pair correlation function was assumed as well as its independence of momentum.

V.2. The Fokker-Planck Equation

The transport theory developed by Kirkwood is mainly based upon the Fokker-Planck equation and the molecular interpretation of the frictional coefficient. The general procedure employed has been to obtain only those moments required by suitable multiplication and averaging of the resultant Fokker-Planck equation. Rather than detail this procedure we turn to an analysis of the Fokker-Planck equation in terms of a general solution and a variational principle. This section is based upon the work of Lebowitz, Frisch & Helfand (69). We restrict attention to the equation of change of the singlet distribution function.

We seek solutions of

$$\frac{\partial \bar{f}^{(1)}}{\partial t} + \frac{p}{m} \cdot \nabla \bar{f}^{(1)} + \frac{1}{m} F \cdot \nabla_c \bar{f}^{(1)} = \zeta \left[\nabla_c \cdot \xi \bar{f}^{(1)} + \frac{kT}{m} \nabla_c^2 \bar{f}^{(1)} \right] \qquad (V.2.1)$$

$$\mathcal{L}\bar{f}^{(1)} = \zeta \mathcal{F} \bar{f}^{(1)}$$

where $\xi = c - u$ is the velocity of the molecules relative to the mean velocity u and $c = p/m$. We assume ζ is independent of momentum and is presumed to be a known function. In terms of the dimensionless variable W,

$$W = \sqrt{\frac{m}{kT}} (c - u) \qquad (V.2.2)$$

The second order differential operator $\mathcal{F}$ may be written

$$\mathcal{F}\bar{f}^{(1)} = \nabla_W \cdot [e^{-W^2/2} \nabla_W (\bar{f}^{(1)} e^{W^2/2})] \qquad (V.2.3)$$

The force F which appears in the Fokker-Planck equation consists of two parts

$$F = -\nabla_R V + \hat{Q}$$

$$Q_i^{(n)} = -\int \nabla_{R_i} V \left[\frac{f^{(n+1)}}{f^{(n)}} \right] dR^{(N-n)} dp^{(N-n)} \qquad (V.2.4)$$

and $\hat{Q}$ is that part of the force $Q_1^{(1)}$, which does not depend on the velocity c. It is easy to verify that if $\bar{f}^{(1)}$ and $\nabla_c \bar{f}^{(1)}$ vanish sufficiently rapidly as $|c| \to \infty$, number density, momentum and kinetic energy are conserved. From these conservation conditions are obtained the usual hydrodynamic equations of motion.

The structure of Equation V.2.1 is not unlike that of the Boltzmann equation and a similar technique may be used to obtain the normal solutions. As might be expected both the Enskog and the Grad (70) procedures yield the same result to terms linear in the gradients of temperature, mean velocity and density. The result is

$$\bar{J}^{(1)} = \bar{J}_o^{(1)} \left[1 + \frac{m p_{ij}}{2pkT} \xi_i \xi_j - \frac{m q_i \xi_i}{pkT} \left(1 - \frac{m\xi^2}{5kT} \right) \right] \tag{V.2.5}$$

in terms of the flows, or

$$\bar{J}^{(1)} = \bar{J}_o^{(1)} [1 - \tau_2 C_2 - \tau_3 C_3] \tag{V.2.6}$$

in terms of the fluxes. The unidentified terms in Equations V.2.5 and V.2.6 are

$$p_{ij} + p\delta_{ij} = m \int \xi_i \xi_j \bar{J}^{(1)} dc$$

$$q_i = \frac{m}{2} \int \xi_i \xi^2 \bar{J}^{(1)} dc$$

$$C_2 = \frac{m}{kT} \left[\xi_i \xi_j - \frac{1}{3} \xi^2 \delta_{ij} \right] \frac{\partial u_j}{\partial x_i} \tag{V.2.7}$$

$$C_3 = \left[\frac{m\xi^2}{2kT} - \frac{5}{2} \right] \xi_i \frac{\partial \ln T}{\partial x_i}$$

$$\tau_2 = \frac{1}{2\zeta}$$

$$\tau_3 = \frac{1}{3\zeta}$$

The method of solution proposed by Grad involves the expansion of $\bar{J}^{(1)}(1)$ in Hermitian polynomials in W. If we put

$$S(W) = e^{-W^2/2} \tag{V.2.8}$$

then the Hermitian polynomials are defined by

$$H_{i_1 \cdots i_n}^{(n)} = \frac{(-)^n}{S(W)} \frac{\partial}{\partial W_{i_1}} \cdots \frac{\partial}{\partial W_i} S(W) \tag{V.2.9}$$

and by reference to Equation V.2.3 we note that these polynomials are the eigenfunctions of $\mathfrak{F}$ with eigenvalue equal to the index of $H^{(n)}$, i.e.,

$$\mathfrak{F}S(W)H^{(n)} = - nS(W)H^{(n)} \tag{V.2.10}$$

Since these eigenfunctions can be shown to form a complete set, their suitability for finding the solution of the Fokker-Planck equation is quite clear. Detailed calculations are presented by Grad and by Frisch and Lebowitz. Here we shall outline the conceptually simpler but mathematically more complicated method of Enskog. To start, write:

$$\mathcal{L}\bar{J}^{(1)} = \frac{1}{\epsilon} \mathfrak{F}\bar{J}^{(1)} \tag{V.2.11}$$

$$\bar{J}^{(1)} = \bar{J}_o^{(1)} + \epsilon \bar{J}_1^{(1)} + \epsilon^2 \bar{J}_2^{(1)} + \cdots \tag{V.2.12}$$

where the formal expansion parameter ϵ will later be set equal to unity. The actual expansion parameter is the variation of the gross variables over the path $c_0 \zeta^{-1}$ where c_0 is a characteristic molecular velocity. By the usual method of substitution and collection of terms it is found that

$$\mathfrak{F}\mathfrak{J}_o{}^{(1)} = 0 \tag{V.2.13}$$

$$\mathfrak{L}\mathfrak{J}_o{}^{(1)}(1) = \mathfrak{F}\mathfrak{J}_1{}^{(1)} \tag{V.2.14}$$

The general solution of V.2.14 is a Maxwell distribution with spread and mean value determined by the local temperature, velocity, and density. Thus,

$$\mathfrak{J}_o{}^{(1)}(1) = n_0(R, t) \left[\frac{m}{2\pi k T_o(R, t)} \right]^{3/2} \exp\left\{ -\frac{m[c - u_o]^2}{2kT_o} \right\} \tag{V.2.15}$$

The main feature of Enskog's method is that the entire time dependence of the distribution function is made to reside in n_o, T_o, u_o. Thus, in the term $\mathfrak{L}\mathfrak{J}_1{}^{(1)}$ the time derivatives $\partial n/\partial t$, $\partial T/\partial t$, $\partial u/\partial t$ can be written in terms of the stress tensor and heat flux. The force F is assumed to be a known function of R.

Now, Equation V.2.1 can be written explicitly as

$$(C_2 + C_3)\mathfrak{J}_o{}^{(1)}(1) = \frac{kT\zeta}{m} \nabla_\xi \cdot \left[\mathfrak{J}_o{}^{(1)} \nabla_\xi \left(\frac{\mathfrak{J}_1{}^{(1)}}{\mathfrak{J}_o{}^{(1)}} \right) \right] \tag{V.2.16}$$

and the solution satisfying the conservation conditions

$$\left. \begin{array}{l} \int \mathfrak{J}_i{}^{(1)} dc = 0 \\[2mm] \int \mathfrak{J}_i{}^{(1)} c\, dc = 0 \\[2mm] \int \mathfrak{J}_i{}^{(1)} c^2 dc = 0 \end{array} \right\} \quad i \geq 1 \tag{V.2.17}$$

is given by

$$\mathfrak{J}_1{}^{(1)} = -\left[\frac{C_2}{2\zeta} + \frac{C_3}{3\zeta} \right] \mathfrak{J}_o{}^{(1)} \tag{V.2.18}$$

The kinetic stress tensor and kinetic heat flux corresponding to this distribution function are

$$q_k = \frac{5nk^2T}{6\zeta} \nabla T \tag{V.2.19}$$

$$\sigma_k = nkT \left[1 - \frac{1}{2\zeta} \left(2\,\dot{\epsilon} - \frac{2}{3} \nabla u \right) \right] \tag{V.2.20}$$

with $\dot{\epsilon}$ the rate of strain tensor. The thermal conductance and shear viscosity (kinetic contributions) are thereby

$$\kappa_k = \frac{5nk^2T}{6m\zeta} \tag{V.2.21}$$

$$\eta_k = \frac{nkT}{2\zeta} \tag{V.2.22}$$

To find the intermolecular force contributions, it is necessary to solve the

equation of change for the pair distribution function. By application of the same techniques, the result is shown to be

$$\bar{f}^{(2)}(R_1 R_2 c_1 c_2; t) = g^{(2)}(R_1 R_2; t) \prod_{i=1}^{2} \left[\frac{n_i m}{2\pi k T_i} \right]^{3/2} \exp\left\{ -\frac{m\xi_1^2}{2kT_1} \right\} \exp\left\{ -\frac{m\xi_2^2}{2kT_2} \right\}$$

$$\times \left[1 - \tau_2(1)C_2(1) - \tau_2(2)C_2(2) - \tau_3(1)C_3(1) - \tau_3(2)C_3(2) \right. \tag{V.2.23}$$

$$\left. - \tau_o(1)\xi_1 \cdot \left(\nabla_1 \ln g^{(2)} - \frac{F_2^{(1)}}{kT_1} \right) - \tau_o(2)\xi_2 \cdot \left(\nabla_2 \ln g^{(2)} - \frac{F_2^{(2)}}{kT_2} \right) \right]$$

and all symbols have been defined previously.

In general, the transport coefficients computed by the use of the Fokker-Planck equation and the approximate formula for the frictional coefficient quoted in the next section are within 50 per cent of the experimental values. The calculation of ζ is particularly troublesome since the integral is very sensitive to the exact form of $g^{(2)}$. The agreement is heartening and should be understood to be preliminary. What is required in part are more extensive data to guide further developments and determine in more detail than just overall nonagreement with one number, the point at which the theory breaks down.

It is pertinent to inquire whether or not the nonequilibrium distribution function is determined by a variational principle. It may be shown (69) that the linear nonequilibrium distribution discussed above maximizes the variable

$$R = S + \frac{1}{3\zeta}\sigma_3 + \frac{1}{2\zeta}\sigma_2$$

$$\sigma_2 = -k \int C_2 \bar{f}^{(1)} d\xi \tag{V.2.24}$$

$$\sigma_3 = -k \int C_3 \bar{f}^{(1)} d\xi$$

The quantities σ_2 and σ_3 are seen to be the entropy productions due to heat flow and momentum flow respectively. The variable R reduces to the entropy, S, when equilibrium is attained and $\sigma_2 = \sigma_3 = 0$. While S is a maximum for $\bar{f}^{(1)} = \bar{f}_o^{(1)}$ the increase in entropy production achieved by a deviation from equilibrium more than offsets the decrease of entropy from its maximum value.

V.3. Approximate Theories for Dense Fluids

In addition to the explicit transport theories based on the Fokker-Planck equation and the Liouville equation there are three recent approximate theories of transport in fluids. Rice & Kirkwood (71) have used a development based on a series expansion in terms of the displacement of a particle in time τ. This technique is related to the use of a diffusion trajectory to

describe the motion of a molecule. Collins, Raffel & Mandel (48, 72) have also developed a theory based on the diffusion trajectory of a molecule, but by different means. Finally, Fixman (73) has approximated the frictional force acting on a molecule by expanding the reaction to the motion of a particle in terms of acoustic waves and their scattering.

Rice & Kirkwood (71) start their analysis by defining the mean force acting on a selected particle, say molecule one, by the relation:

$$\langle F_1 \rangle = \frac{(N-1)v}{\tau} \int \left[\int \int_0^\tau \nabla_{R12} V(R_{12}(t+s)) f^{(N)}(t) \delta(R_1^\circ - R_1) \right.$$
$$\left. \times \delta(R_2^\circ - R_2) ds dR^{(N)} dp^{(N)} \right] dR_2^\circ \qquad (V.3.1)$$

Since the potential energy is not an explicit function of time, but depends upon t only through the change in intermolecular separation with time, a useful expansion is embodied in

$$\nabla_{R_{12}} V(R_{12}(t+s)) = \nabla_{R_{12}} V(R_{12}(t)) + \Delta R_{12}(s) \cdot \nabla_{R_{12}} \nabla_{R_{12}} V(R_{12}(t)) + \cdots$$
$$R_{12}(t+s) = R_{12}(t) + \Delta R_{12}(s) \qquad (V.3.2)$$

The neglect of higher order terms will be valid if $\Delta R(s)$ is small or $\nabla\nabla V$ is small. While no *a priori* judgment can be made, considerations based on simple cell models suggest that $(\Delta R)^2 \nabla\nabla V$ is negligible relative to $\Delta R \nabla\nabla V$. To explicitly calculate the mean force $\langle F_1 \rangle$ Rice and Kirkwood assumed the following form for the pair distribution function,

$$f^{(2)} = \frac{g_o^{(2)}(R_{12})}{v^2} \frac{e^{-p_{12}^2/mkT}}{(\pi mkT)^{3/2}} \left(1 + \frac{p_{12} \cdot u_{12}}{kT}\right) = f_o^{(2)} \left(1 + \frac{p_{12} \cdot u_{12}}{kT}\right) \qquad (V.3.3)$$

from which it is easily shown that

$$\langle F_1 \rangle = \left[\frac{(N-1)v}{3kT\tau} \int \overline{p_{12} \cdot \Delta R_{12}(s)}^{\tau, 12} \nabla^2 V f_o^{(2)} dp_1 dp_2 dR_{12} \right] u_{12} \quad (V.3.4)$$

$$\overline{p_{12} \cdot \Delta R_{12}(s)}^{\tau, 12} = \int_0^\tau p_{12} \cdot \Delta R_{12}(s) f^{(2/N-2)} dR^{(N-2)} dp^{(N-2)} ds \qquad (V.3.5)$$

and where u_{12} is the relative fluid velocity. By use of the linear relation between the frictional force and the relative velocity

$$\langle F_1 \rangle = \zeta u_{12} \qquad (V.3.6)$$

and changing the variable of integration in V.3.5 from ds to $d\Delta R_{12}(s)$ we find

$$\zeta^2 = \frac{Nm}{3v} \int \nabla_{R_{12}}^2 V(R_{12}) g_o^{(2)}(R_{12}) d^3 R_{12} \qquad (V.3.7)$$

In obtaining V.3.7 it has also been assumed that the pair diffusion tensor is approximately the direct sum of the singlet diffusion tensors of the single molecules. By use of the definition $\mathfrak{D} = kT/\zeta$, Equation V.3.7 provides a relationship between the coefficient of self diffusion and the intermolecular

forces. Rice (98) has derived Equation V.3.7, except for a numerical factor of $(2/\pi)$, from the autocorrelation function definition of the diffusion coefficient. This numerical factor greatly improves agreement with experiment and the derivation of the general form of the result by still another method adds to the conviction that the analytical form of Equation V.3.7 is correct.

Starting from the general theoretical formulae for the stress tensor and heat flux given by Irving and Kirkwood, it is possible to show by exactly the same means as illustrated above that (71, 74)

$$\eta_V = \frac{m}{30\zeta}\left(\frac{N}{v}\right)^2 \int R_{12}^2\left[V'' + \frac{4V'}{R_{12}}\right]g_o{}^{(2)}(R_{12})d^2R_{12}$$

$$\phi_V = \frac{m}{18\zeta}\left(\frac{N}{v}\right)^2 \int R_{12}^2\left[V'' + \frac{V'}{R_{12}}\right]g_o{}^{(2)}(R_{12})d^2R_{12} \qquad (V.3.8)$$

$$\kappa_V = -\frac{kT}{12\zeta}\;\frac{\partial}{\partial T}\left(\frac{N}{v}\right)^2 \int R_{12}^2\left[V'' + \frac{2V'}{R_{12}}\right]g_o{}^{(2)}(R_{12})d^3R_{12}$$

Since all the transport coefficients are expressed in terms of $\mathfrak{D}$ (or ζ) and equilibrium properties of the fluid, it is convenient to evaluate the integrals in terms of known thermodynamic functions. For the Lennard-Jones 6–12 potential the results are

$$\eta_V = \frac{3m\mathfrak{D}}{5kTv}\left[8L + 5pv - 5RT\right]$$

$$\phi_V = \frac{2m\mathfrak{D}}{vkT}\left[4L + 3pv - 3RT\right] \qquad (V.3.9)$$

$$\kappa_V = \frac{3\mathfrak{D}}{v}\left[8\Delta C_p - 15R - 5pv\alpha\right] + \frac{5kT\alpha}{m}\eta_V + \frac{\mathfrak{D}R}{v}\left[1 - \alpha T\right]$$

with α the coefficient of thermal expansion and L the potential energy of the fluid. A comparison of Equation V.3.9 with experiment will be deferred until later in this section.

An entirely different formalism has been developed by Collins and coworkers (72) for the discussion of transport properties in liquids. The approach is based on the fluctuation ensembles discussed previously. The primary step in this theory requires the expression of the time derivative of the nonequilibrium stresses in terms of the gradient of the property being transported. This time derivative of a macroscopic property introduces the irreversibility via a fluctuation ensemble. We shall see that another assumption is used that is concerned with the mode of decay of a fluctuation and plays the role of time smoothing by an equivalent but probably less exact extrapolation of the steady state.

Consider a Gibbs ensemble of copies of the liquid system corresponding to a state of macroscopic equilibrium. From this ensemble we select all those replicas having a molecule with velocity between p_1^0/m and $(p_1^0+dp_1)/m$ and a position at the time t_o within the volume element $d R_1^0$ located at R_1^0. The

volume element $(1/m)d\boldsymbol{p}_1{}^0 d\boldsymbol{R}_1{}^0$ is taken to be small, but finite, so that it contains a large number of molecules, one from each of an arbitrary M replica system. The M replica systems may then be considered to form a subensemble, the average behavior of which represents the mean behavior of a system in a state of equilibrium except for one molecule having a known velocity and position. Note that in this fluctuation ensemble we have fixed a microscopic set of variables and irreversibility is yet to be introduced.

If there is no external force acting on the system, then $\langle \boldsymbol{p}_1 \rangle = 0$ where we define the subensemble average velocity by

$$\frac{1}{m} \langle \boldsymbol{p}_1 \rangle = \frac{1}{mM} \sum_1^M \boldsymbol{p}_{1\mu} \tag{V.3.10}$$

where $\boldsymbol{p}_{1\mu}$ is the momentum of the given molecule in the μth replica system. Now assume that the ensemble average force acting on the central molecule is

$$\langle \boldsymbol{F}_1 \rangle_{t_0} = -\frac{\zeta}{m} \boldsymbol{p}_1{}^0$$

$$= -\frac{\zeta}{m} \langle \boldsymbol{p}_1 \rangle_{t_0} \tag{V.3.11}$$

where $\langle \boldsymbol{F}_1 \rangle_{t_0}$ is defined by a relation analogous to V.3.10. Note that although written in terms of the velocity of molecule 1, Equation V.3.11 really refers to the relative mean velocity of molecule one and any other molecule when at $\boldsymbol{R}_1$. However, since all the other molecules are, by hypothesis, at equilibrium, the second average velocity is equal to zero. Irreversibility is introduced at this point by the assumption of the existence of the frictional coefficient ζ, and corresponding frictional force.

By differentiation with respect to time

$$\left\langle \frac{d\boldsymbol{F}_1}{dt} \right\rangle_{t_0} = -\frac{\zeta}{m} \left\langle \frac{d\boldsymbol{p}_1}{dt} \right\rangle_{t_0} \tag{V.3.12}$$

since

$$\frac{d}{dt} \left(\frac{1}{M} \sum_1^M \boldsymbol{F}_{1\mu} \right) = \frac{1}{M} \sum_1^M \frac{d\boldsymbol{F}_{1\mu}}{dt} \tag{V.3.13}$$

Equation V.3.13 asserts that the time derivative of the subassembly average of a dynamical variable of the selected molecule is equal to the subassembly average time derivation of this variable. This implicitly assumes that the subassembly is closed and no replicas are added or removed.

Now, by Newton's second law

$$\langle \boldsymbol{F}_1 \rangle_{t_0} = \left\langle \frac{d\boldsymbol{p}_1}{dt} \right\rangle_{t_0} \tag{V.3.14}$$

so that by combining V.3.11, V.3.12, and V.3.13 we obtain

$$\left\langle \frac{d\boldsymbol{F}_1}{dt} \right\rangle_{t_0} = \frac{\zeta^2}{m^2} \langle \boldsymbol{p}_1 \rangle_{t_0} = \frac{\zeta^2}{m^2} \boldsymbol{p}_1{}^0 \tag{V.3.15}$$

a result that may be generalized to other times simply by dropping the t_o. Equation V.3.15 expresses the instantaneous average time derivative of the force acting on a molecule with the given momentum p_1^o without the necessity of following the behavior of the subassembly over a finite interval of time.

Let us examine closely the meaning of Equations V.3.11 and V.3.14. Consider the mean momentum of molecule 1 as a function of time, averaged over the subassembly. It will look something like Figure V.3.1. We note that the curvature of any function is related to the second derivative. The use
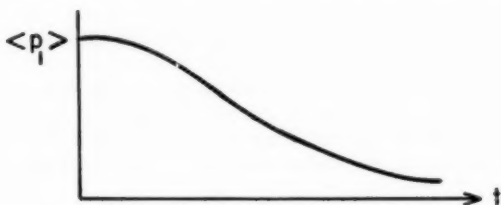
Fig. V.3.1

of Equations V.3.11 and V.3.14 is equivalent to the assumption that the curvature at the origin (in time) is equal and opposite in sign to the curvature in the steady state region. For Equation V.3.14, which is a dynamical relation, holds only when $t \to t_o$ since when $t \geq t_o$ the influence of the environment as expressed in the frictional coefficient, ζ, must be accounted for. Equation V.3.11, on the other hand, holds only in the steady state region after the transients have died down. This assumption is, therefore, equivalent to the extrapolation of the steady state behavior obtained by time smoothing. While the assumption is not implausible as a first approximation there appears to be no *a priori* reason to believe it particularly accurate. We can partially test its accuracy by computing the transport coefficients.

To proceed with a molecular theory we must evaluate $\langle dF_1/dt \rangle$. As usual, assume that

$$V = \sum_{i>j} \sum u_{ij}$$

$$F_{12} = -\nabla_{R_{12}} V \qquad (V.3.16)$$

and thereby

$$\langle F_1 \rangle = \int \nabla_{R_{12}} V f^{(2/1)}(p_2 R_2 / p_1 R_1) dp_2 dR_2 \qquad (V.3.17)$$

where the pair distribution function $f^{(2)}$ is conditioned by the requirement that molecule one have momentum p_1 and position R_1. Thus,

$$f^{(2/1)}(R_2 p_2/R_1 p_1) = \frac{f^{(2)}(R_1 R_1 p_1 p_2)}{f^{(1)}(R_1 p_1)} \qquad (V.3.18)$$

We may now rewrite V.3.17 and take a derivative with respect to time,

$$\left\langle \frac{dF_1}{dt} \right\rangle = \int \frac{d}{dt} \nabla_{R_{12}} V f^{(2/1)} dp_2 dR_2 = - \int \nabla_{R_{12}} \nabla_{R_{12}} V \cdot \frac{p_2 - p_1}{m} f^{(2/1)} dp_2 dR_2 \qquad (V.3.19)$$

It is plausible to assume (as we have already done in the frictional Equation V.3.10) that the distribution of the momentum p_2 is not affected significantly by the condition that the first molecule has momentum p_1. The ensemble average of p_2 then vanishes and,

$$\left\langle \frac{dF_1}{dt} \right\rangle = \frac{1}{m} \int \nabla_{R_{12}} \nabla_{R_{12}} V \cdot p_1 \rho^{(2/1)}(R_2/p_1 R_1) dR_2 \qquad (V.3.20)$$

The conditional configurational pair distribution function, $\rho^{(2/1)}$, differs from the equilibrium value only due to the non-spherical distribution of p_1. For small p_1 we assume the perturbation to be small and use the equilibrium pair density. Now replacing the variable of integration by R_{12}, we have

$$\zeta^2 = \frac{4\pi m}{3} \int_0^\infty \left[V'' + \frac{2V'}{R_{12}} \right] \rho_0^{(2/1)} d^3 R_{12} \qquad (V.3.21)$$

which is the same as the relation given by Kirkwood, Buff & Green (75), and derived by Rice & Kirkwood (71) in the preceding arguments.

Numerical computation of the diffusion coefficient

$$\mathfrak{D} = \frac{kT}{\zeta} \qquad (V.3.22)$$

reveals an unfortunate sensitivity to $\rho_0^{(2/1)}$, or in more familiar terms to $g_0^{(2)}$ where

$$g_0^{(2)} = \frac{\rho^{(2/1)}}{\rho^{(1)}} \qquad (V.3.23)$$

Using a pair correlation function based on the x-ray diffraction data of Eisenstein and of Gingrich (76), and a Lennard-Jones 6, 11.4 potential with $\epsilon = 6.82 \times 10^{-14}$ erg and $a = 3.43$ A, Collins finds $\zeta = 4.84 \times 10^{-10}$ gm. sec.$^{-1}$ at 89° K. and 1.2 atm. pressure. Using a 6–12 potential with $\epsilon = 1.653 \times 10^{-11}$ erg and $a = 3.405$ A, $\zeta = 1.21 \times 10^{-10}$ gm. sec.$^{-1}$, whereas the experimental data of Corbett & Wang (77) give $\zeta = 5.93 \times 10^{-10}$ gm. sec.$^{-1}$ It is interesting that the dominant contribution of ζ comes from the repulsive region of the potential, partially explaining the utility of hard sphere models.

To discuss shear viscosity and thermal conduction, a special form of the hydrodynamic theory is developed in which the dissipative stress and its time derivative are expressed on a per molecule basis. Consider the dynamical property B which is defined in terms of an ensemble average. We wish the rate of transport of B across the bounding surface S of a closed region R in the liquid. By hypothesis the stress on the surface element dS at R_0 is

proportional to the gradient in B for small departures from equilibrium

$$\sigma = -\lambda \nabla B \cdot n \tag{V.3.24}$$

where λ is the transport coefficient for the property B. We now construct a subensemble simulating the behavior of a single molecule under nonequilibrium conditions. From the equilibrium ensemble we will construct a fluctuation ensemble in which that molecule closest to some arbitrary point in the system has a value of the property B lying between $B(R_o) + (R_1 - R_o) \cdot \nabla B$ and $B(R_o) + (R_1 - R_o) \cdot \nabla B + \delta B$ where R_1 is the position of the molecule and the interval δB is small but finite so that the subassembly will contain a large number of replicas. The property B at R_o is taken to be the ensemble average of B for the $N-1$ remaining molecules of the system, and ∇B may have any value but must always be small enough that Equation V.3.24 is followed.

The molecule closest to the point R_o in each of the several replicas is independent of the corresponding molecule in the other replicas and, therefore, their spatial distribution is uniform. The number density $n(R)$ of the molecule closest to some arbitrary point R_o in a collection of randomly distributed molecules is

$$n(R) = \frac{4\pi R^2}{v} e^{-4\pi R^3 / 3v} \tag{V.3.25}$$

where $R = R_1 - R_o$. The surface element dS, with respect to which we are calculating the transport of B is placed at R_o. The mean component difference of the property B in the direction of the normal n is given by

$$\langle \Delta B_n \rangle = 2 \int_o^\infty \int_o^{\pi/2} \int_o^{2\pi} (\nabla B \cdot n R \cos \theta) e^{-4\pi R^3 / 3v^2} \frac{R^2}{v} \sin \theta \, d\phi d\theta dR \tag{V.3.26}$$

where the Z axis of the spherical polar coordinates is along n. The factor 2 arises because ΔB_n changes sign when θ passes $\pi/2$. By direct integration of V.3.26

$$\langle \Delta B_n \rangle = \frac{1}{2} \left(\frac{3}{4\pi} \right)^{1/2} v^{1/3} \Gamma(4/3) \nabla B \cdot n \tag{V.3.27}$$

where $\Gamma(x)$ is the usual gamma function. Now, the expectation value of the area of a plane normal to n at R_o is given by

$$\langle S_1 \rangle = 2 \int_o^\infty \int_o^{\pi/2} \int_o^{2\pi} (\pi R^2) e^{-4\pi R^3 / 3v} \frac{R^2}{v} \sin \theta \left(\theta - \frac{\pi}{2} \right) d\phi d\theta dR$$
$$= \frac{\pi}{2} \left(\frac{3}{4\pi} \right)^{2/3} v^{2/3} \Gamma(5/3) \tag{V.3.28}$$

We therefore have for the mean value of the normal component of the molecular property difference ΔB_n relative to the expectation value of the molecular surface area, the relation

$$\left\langle \frac{\Delta B_n}{S_1} \right\rangle = 0.694 v^{-1/3} \nabla B \cdot n$$

$$\frac{\langle \Delta B_n \rangle}{\langle S_1 \rangle} = 0.510 v^{-1/3} \nabla B \cdot n \tag{V.3.29}$$

A unit area of the plane tangent to dS is $Bv^{-2/3} \langle S_1 \rangle$, $Bv^{-2/3}$ being the expectation number of molecular volumes cut by the tangent plane. However, the quantity $\langle \Delta B_n \rangle$ is increased by the same factor so that V.3.29 gives the mean normal component of the difference in B per unit area.

We now assert the stress to be given by:

$$\sigma = \frac{d}{dt} \left\langle \frac{\Delta B_n}{S_1} \right\rangle = 0.694 v^{-1/3} \frac{d}{dt} \nabla B \cdot n \tag{V.3.30}$$

The time derivative of Equation V.3.24 is

$$\frac{d\sigma}{dt} = -\lambda \frac{d}{dt} \nabla B \cdot n \tag{V.3.31}$$

so that by combination of Equations V.3.24, V.3.30, and V.3.31

$$\frac{d\sigma}{dt} = 1.443 v^{1/3} \lambda^2 \nabla B \cdot n \tag{V.3.32}$$

Note that we have again used the equality of curvature assumption. Equation V.3.32 represents, with the indicated assumptions, the rate of change of the stress due to the dissipative effect in an ensemble at equilibrium save for one molecule.

By consideration of the transport of momentum and energy and identification of terms in the Newtonian stress tensor and the Fourier law of heat conduction, Collins finds (72)

$$\eta v^2 = 0.174 \frac{\pi}{15} \rho_m v^{-4/3} \int_0^\infty (R^4 V'' + 9R^3 V') g_o^{(2)}(R) dR \tag{V.3.33}$$

$$= 0.174 \rho_m v^{-1/3} [2.4L - kT + pv]$$

$$\phi v^2 = 0.694 \frac{2\pi}{q} \rho_m v^{-4/3} \int_0^\infty (R^4 V'' + 3R^3 V') g_o^{(2)}(R) dR \tag{V.3.34}$$

$$\kappa v^2 = 0.694 \frac{4\pi}{3} k C_V v^{-1/3} \int_0^\infty (\alpha T R^4 V'' + (3\alpha T + 1) R^3 V') g_o^{(2)}(R) dR \tag{V.3.35}$$

$$= 0.694 k C_V v^{-4/3} [20\alpha T L - (14\alpha T - 1) kT]$$

where

$$g_o^{(2)} = v \rho^{(2/1)}$$

$$\rho_m = m \rho^{(1)}$$

and the other symbols have their usual meanings. The second relations for ηv^2 and κv^2 arise when the equation of state is used to eliminate the unknown integrals as in the previous section.

The major differences between the approaches in Sections I and 2 arise from the method of introducing the irreversibility. Collins used a more accurate approximate distribution function than did Rice and Kirkwood. Note that Collins' theory gives the squares of transport coefficients consistently, whereas the other gives first powers, except for ζ.

It is of interest to examine the agreement between experiment and theory as shown in Table V.3.1. The agreement is quite satisfactory, especially with regard to the calculations of Rice and Kirkwood assuming $\mathfrak{D}$ and η or $\mathfrak{D}$ and κ are known and calculating the third coefficient.

<center>TABLE V.3.1</center>

Experimental	2.39×10^{-2} poise	2.90×10^{-4} cal./o	2.07×10^{-5} cm.^{2}/sec.
Collins, Raffel, &			
Mandel*	1.28×10^{-2}	0.645×10^{-4}	4.90×10^{-5}
Rice & Kirkwood	1.33×10^{-2}	1.64×10^{-4}	2.60×10^{-5}
Rice & Kirkwood†			
(semi-empirical)	2.37×10^{-2}	2.87×10^{-4}	

* For the 6–12 potential.

† Taking $\mathfrak{D}$ and η or $\mathfrak{D}$ and κ as known and computing the third of the coefficients.

Consider now the approximations used in the Rice-Kirkwood theory.

The effects of neglecting third and higher order terms in the expansion of the gradient of the pair potential at time $t+s$ about the gradient at time t can only be rigorously assessed when an exact statistical mechanical theory of transport is developed. Nevertheless, some intuitive notions, while not rigorous, are worth discussing. The expansion used would be rigorously correct if the displacement forces of an atom obeyed Hooke's law, when third and higher order derivatives are identically zero. The expansion used would also be accurate if the length of a diffusive motion, $\Delta R(s)$, was very small, since then the higher powers of $\Delta R(s)$ would annihilate any contribution from derivatives of the pair potential. We may cite the following physical inferences to support the proposition that both $\nabla^3 V$ and ΔR are small. It is important to note that these inferences are based on incorrect models and should not be considered as more than order of magnitude indications. If the self-diffusion coefficients of liquids are forced into the activated state model of diffusion, and the effective jump frequency estimated via the specific heat, then the length of a diffusive displacement is of the order of magnitude of one-tenth a nearest neighbor distance for all the liquids studied (78). Within the framework of the activated state mode, $\Delta R(s)$ cannot be large, or any consistency with thermodynamic properties is lost. In the same vein and in fact closely related, the cell model for liquids gives good agreement with the energy of a fluid, poor agreement with the entropy, while using essentially a harmonic oscillator model. The entropy disagreement can

be largely removed by considering correlations in the motions of nearby atoms, even in the cell approximation. This would tend to indicate that $\nabla^3 V$ is small relative to $\nabla^2 V$. While both the estimates of ΔR and $\nabla^3 V$ may be in considerable error, the above arguments point to the probability that the product $1/2(\Delta R)^2 \nabla^3 V$ is small relative to the terms retained.

The fact that the distribution function in pair space is approximated as the product of the local equilibrium distribution function in configuration space and the zeroth order distribution function in momentum space is probably the mildest of the approximations we have made. In the gaseous state, the zeroth order contributions to the stress tensor and heat flux are dominant, and the higher terms amount to small corrections of the order of magnitude of ten per cent or less.

The diffusion tensor in pair space can always be approximated as the direct sum of the diffusion tensors (diagonal) in singlet space if the pair separation is large. How close a pair of molecules must be before this breaks down is unknown. It should be noted that this additivity approximation is equivalent to decoupling the molecules at all distances. This is very much like the approximations involved in the cell model and the activated state model of diffusion mentioned above. Again, rigorous justification must await a more complete theory.

Where the techniques of the Collins, Raffel, and Mandel theory overlap those of Rice and Kirkwood, a similar analysis of the approximations can be made. In general, however, the technique of introducing irreversibility is sufficiently different to require new analysis. Objections have been raised that the curvature assumption used violates the condition of microscopic reversibility. Collins and Mandel have attempted to answer these objections, but in our opinion they have not succeeded in doing so. Collins & Mandel (48) have suggested a method for determining if the frictional coefficient is velocity dependent. Their analysis introduces a mean correlation length, the analogue of the mean free path in the theory of gases.

An expansion of the frictional coefficient in powers of the mean velocity and subsequent expansion of the pair distribution function about the point $R_1 - \lambda_o$, where λ_o is the mean correlation length, leads to

$$\langle \zeta \rangle = \zeta + \frac{3\pi m^2 kT}{10 v \zeta^3} \int R^2 \left[V'''' + \frac{4V'''}{R} \right] g_o^{(2)} dR$$

$$\lambda_o = \frac{m}{\zeta} \left\langle \frac{p_1}{m} \right\rangle \tag{V.3.36}$$

$$\langle \lambda_o \rangle = \frac{m}{\langle \zeta \rangle} \left(\frac{8kT}{\pi m} \right)^{1/2}$$

It is claimed that use of the above expansion leads to improved accuracy in the computation of the self diffusion coefficient. With a 6–11.4 potential Collins and Mandel obtain $\langle \zeta \rangle = 5.55 \times 10^{-10}$ gm. sec.$^{-1}$, whereas $\zeta = 4.84$

$\times 10^{-10}$ gm. sec.$^{-1}$ for the same potential. The experimental value of Corbett and Wang is $\zeta_{exp} = 5.93 \times 10^{-10}$ gm. sec.$^{-1}$.

The Collins-Mandel development of the mean correlation length, while far from rigorous, is very suggestive. It is not clear that consistency can be maintained between the Fokker-Planck point of view with a momentum dependent frictional coefficient and the basic considerations advanced by Kirkwood. Since the above development deals only casually with many of the fundamental problems of transport theory, much further work is necessary before definitive conclusions can be drawn.

We turn now to an examination of Fixman's (73) approach to the study of transport phenomena in fluids. The arguments begin with a formal treatment of the theory of regression of fluctuations in an equilibrium ensemble. The basic assumption in the analysis is that a macroscopic flux $\bar{\gamma}_i(R_1)$ at the point R_1 is related to a fluctuation $\phi_k(R_2)$ at R_2 by the equation

$$\bar{\gamma}_i(R_1) = \sum_k \int L_{ik}(R_{12})\phi_k(R_2)dR_2 + E_i(R_1) \qquad (V.3.37)$$

where $\bar{\gamma}_i$ is the average of the instantaneous flux over a time interval τ sufficiently large that the flux reaches a steady state. L_{ik} is assumed to be a function only of the separation of the two points R_1 and R_2 and is, in general, a differential operator. Finally, $E_i(R_1)$ is an error term that completes the description of the flux and is assumed to be linear in the fluctuations. The differential operator L_{ik} is determined by minimization of $\langle [\int_{\delta v} E_i(R_1)dR_1]^2 \rangle$ where δv is a small volume element with the result that

$$\langle \bar{\gamma}_i(R_1)\phi_k(R_2) \rangle = \sum_l \int L_{il}(R_{12})\langle \phi_k(R_2)\phi_l(R_3) \rangle dR_3 \qquad (V.3.38)$$

Now consider the series development

$$L_{ik}(R_{12}) = A_{ik}\delta(R_{12}) - B_{ik}\cdot\nabla_{R_2}\delta(R_{12}) + \cdots \qquad (V.3.39)$$

From which the mean flux is found to be

$$\gamma_i(R_1) = - \sum_k B_{ik}\cdot\nabla_{R_1}\phi_k(R_1)$$

$$B_{ik} = \sum_l \int (R_1 - R_2)\langle \bar{\gamma}_i(R_1)\phi_l(R_2) \rangle \frac{|\Phi(0)|_{lk}}{|\Phi(0)|} dR_2 \qquad (V.3.40)$$

$$\Phi_{lk} = \int \langle \phi_k(R_2)\phi_l(R_1) \rangle dR_1$$

and $|\Phi(0)|_{lk}$ and $|\Phi(0)|$ are respectively the cofactor and determinant of the matrix formed by the Φ_{lk}.

Equation V.3.40 is identical in form to the macroscopic equations of transport with the exception that the fluxes are asserted to be proportional to the gradients of the fluctuations in the quantities which give rise to the fluxes rather than the quantities themselves. However, since the gradient of the mean quantity is zero, the two are seen to be identical in content.

The coefficients B_{ik} are essentially transport coefficients and can be evaluated in terms of molecular parameters. Fixman has shown that the introduction of molecular formulae for the fluxes and fluctuations leads, via Equation V.3.40, to the general relation

$$B_{ik} = \sum_{l} \sum_{m,n,t} \frac{1}{v} \langle (R_m - R_l{}^o) h_l(R_{mn}, p_m) g_l(p_t{}^o) \rangle^\tau \frac{|\Phi(0)|_{ik}}{|\Phi(0)|}$$

where the summation over m, n, and t refers to specific molecules in the fluid and the averaging is over the initial coordinates and momenta and the time average is over an interval τ. The time average follows the average over initial conditions. The result quoted follows from the general form of the fluxes and fluctuations,

$$\bar{\gamma}_i(R_1) = \sum_{m,n} \delta(R_1 - R_m) h_i(R_{mn}, p_m)$$

$$\phi_l(R_2) = \sum_{t} \delta(R_2 - R_t) g_l(p_t)$$

along with the assumption that the correlation in Equation V.3.40 is a function only of $|R_{12}|$. The functions h_i and g_l differ for the various fluxes and fluctuations.

Consider now the magnitude of the time interval τ necessary to establish steady state fluxes. Fixman studies this problem by applying the theory to the calculation of the coefficient of shear viscosity for a dilute gas. For this case,

$$\hat{e}_y \eta = mB$$

$$\frac{vkTm^2}{N} B = - \langle (R_1 - R_1{}^o) p_1{}^x p_1{}^y p_1{}^{ox} \rangle^\tau - N \langle (R_1 - R_2{}^o) p_1{}^x p_1{}^y p_2{}^{ox} \rangle^\tau \quad (V.3.43)$$

and $\hat{e}_y$ is the unit vector in the y direction. As before, the superscript τ denotes a time average over the interval $0 \le t \le \tau$.

Detailed evaluation of V.3.43 requires the introduction of the properties of either the real or model fluid. The choice of correct model is a difficult problem. Fixman has proposed an extremely interesting model in which the transfer of momentum between molecules in the gas occurs by the propagation of acoustic waves between them. First, note that for times long compared to a molecular collision time, the first term on the right hand side of V.3.43 vanishes because correlation is lacking between position and momentum of a Brownian particle when τ is large. Now as τ increases, $|R_1 - R_2{}^o|$ increases. Thus we seek a correlation mechanism such that the value of the momentum of molecule 2 initially can be conveyed to a distant point in the fluid (R_1). Fixman assumes that the correlation may be accomplished by the propagation of acoustic waves. $3N$ spherical acoustic waves, 3 for each molecule, are chosen. The waves propagate into or out from a selected molecule, and the random force $X(t)$ of Brownian motion theory is assumed to

be the acoustical force acting on a molecule as a result of fluid compression in the neighborhood of the molecule. More precisely, from

$$\frac{dp_i}{dt} = -\beta p_i + {}_iX(t) \tag{V.3.44}$$

and applying the Fourier transform operator to both sides of V.3.44 we obtain

$$-i\omega A_\omega{}^i = -\beta A_\omega{}^i + X_\omega{}^i \tag{V.3.45}$$

for the transformed equation of motion.

Fixman now modifies the usual laws of Brownian motion so as to introduce a correlation between distant molecules. If $V_\omega{}^{(2)}(R_1)$ is the Fourier component of the momentum of a fluid at a point R_1 relative to the center of a vibrating source at the position of molecule 2 (the local fluid momentum being derived from a potential $\psi_\omega{}^{(2)}(R_1)$ satisfying the wave equation) we modify V.3.45 to read

$$-i\omega A_\omega{}' = -\beta[A_\omega{}' - V_\omega{}^{(2)}(R_1)] + X_\omega{}' \tag{V.3.46}$$

Equation V.3.46 explicitly states that a frictional force is exerted on molecule 1 as a result of the knowledge of the motion of molecule 2. The result of Fixman's analysis is that the time smoothing interval, τ may be infinite. For the dilute gas, Fixman finds

$$v_\eta = Nm\mathfrak{D}$$

which is 20 per cent higher than the result of Chapman-Enskog theory.

V.4. Principle of Corresponding States for Transport Properties (99)

Principles of corresponding states have long been known and applied to both equilibrium and transport properties of pure materials (79). One means of derivation proceeds by dimensional analysis with either the critical constants or appropriate combinations of molecular parameters commonly used for the reduction of variables. Pitzer (80) has detailed a set of assumptions that allows the partition function to be cast into a reduced variable form, thus providing a statistical mechanical proof of the law of corresponding states for thermostatic properties. In essence, it is required that the intermolecular pair potential of all molecules be of the form $V = \epsilon V^*(R/\sigma)$ where ϵ and σ are characteristic energy and distance constants and V^* is a universal function of the one variable R/σ. Thus, the simple law of corresponding states may be expected to hold for spherical nonpolar molecules if, for instance, the potential is of the Lennard-Jones 6–12 type. Introduction of additional parameters, such as a reduced dipole moment, into the equation of state extends the validity of the principle of corresponding states, although this sometimes limits its utility.

Pitzer originally limited consideration to systems whose translational degrees of freedom are classical and internal degrees of freedom are unexcited.

The translational restriction may be removed (81) by introducing a reduced Planck constant as a parameter, leading to a mass dependence of the thermodynamic properties. Aside from providing the basis for extension of the law of corresponding states to nonspherical potentials and quantum systems, the Pitzer technique of reducing the partition function has also been useful in deriving conformal solution theory.

It is possible to show that with the intermolecular potential of the form suggested by Pitzer, a law of corresponding states can be derived for the transport coefficients. The demonstration will be based on the use of expressions for the transport coefficients in terms of time integrals of appropriate auto-correlations functions.[8] Such equations have been derived by Kubo, Yokota & Nakajima (82) by consideration of the regression of fluctuations, which are assumed to follow the macroscopic laws; and by Mori (83), who assumes that a local equilibrium distribution will relax rapidly to the stationary state. The rigorous demonstration of the theorem of corresponding states presented herein validates the dimensional analysis ordinarily used.

The important point in our proof of the law of corresponding states will be that in addition to the distribution function, the solution of the mechanical equation of motion may be written in reduced variables. The principles are demonstrated for the shear viscosity in the quantum mechanical case. The classical results, of course, follow in the limit $h \to 0$. The bulk viscosity, thermal conductivity, and self-diffusion constant will be briefly discussed and the results stated.

The shear viscosity is given by the formula

$$\eta = \frac{1}{v} \frac{\int_0^\infty dt \int_0^{1/kT} d\lambda \, Tr\{J_{xy}(v) e^{i(t+i\lambda\hbar/2\pi)H/\hbar 2\pi} J_{xy}(v) e^{-i(t+i\lambda\hbar/2\pi)H/\hbar 2\pi} e^{-H/kT}\}}{Tr\{e^{-H/kT}\}}$$

Consider the reduced variables

distance:	$r^* = r/\sigma$	(V.4.2)
mass:	$m^* = m/m = 1$,	(V.4.3)
pair potential:	$u^*(r^*) = u/\epsilon$.	(V.4.4)

From this basic set we find the reduced quantities:

temperature:	$T^* = Tk/\epsilon$, $(k^* = 1)$	(V.4.5)
time:	$t^* = t\epsilon^{1/2}/m^{1/2}\sigma$,	(V.4.6)
momentum:	$p_i = p_i m^{1/2}\epsilon^{1/2}$,	(V.4.7)
volume:	$v^* = v/\sigma^3$,	(V.4.8)

[8] The principle of corresponding states may also be established by consideration of other formulations of the transport coefficients. A particularly transparent form is given by Rice & Kirkwood (87), where the thermal conductivity and viscosities are expressed in terms of the self-diffusion coefficient. In this case, only reduced temperature, volume, and pressure are required to obtain the reduction.

pressure: $\qquad p^* = p\sigma^3/\epsilon,$ (V.4.9)

Planck constant: $\qquad h^* = \hbar/\sigma m^{1/2}\epsilon^{1/2},$ (V.4.10)

$J^{(v)}$ tensor: $\qquad J^{(v)*} = J^{(v)}/\epsilon, = \sum_i (p_i^* p_i^* + r_i^* F_i^*) - p^* v^* 1$ (V.4.11)

(where F_i is the force on i), and Hamiltonian:

$$H^* = H/\epsilon = \sum_i \left[\frac{1}{2}(p_i^*)^2 + \sum_j' u^*(r_{ij}^*) \right]$$ (V.4.12)

The reduced Hamiltonian is a universal function of the momentum and position operators so that for any particular reduced volume (which enters through the boundary conditions) there is a universal set of reduced eigenfunctions and energy levels.

The use of Equations V.4.2 to V.4.12 in Equation V.4.1 results in the reduction

$$\eta^* = \eta\sigma^2/\sqrt{m\epsilon}$$ (V.4.13)

where η^* is given by Equation V.4.1 with a reduced variable replacing each unreduced variable. It is easily seen, for instance, that in an energy diagonal representation the reduced viscosity is a universal function of reduced temperature, pressure, and Planck's constant; i.e.,

$$\eta^* = \eta^*(T^*, p^*, h^*)$$ (V.4.14)

where use of the correspondence equation of state, $v^* = v^*(T^*, P^*, h^*)$ has been made.

It is pertinent to reiterate that: (a) the density matrix has the reduced form $\exp[-H^*/T^*]/Tr\{\exp[-H^*/T^*]\}$, and (b) the similarity transform with reduced unitary operator $\exp[-i(t^*+ih^*\lambda^*)H^*/h^*]$ formally represents a reduced solution of the equations of motion, albeit in complex time.

The bulk viscosity differs from Equation V.4.1 only in involving diagonal elements of the $J^{(v)}$ tensor. The correct reduction therefore is also

$$\phi^* = \phi\sigma^2/\sqrt{m\epsilon}$$ (V.4.15)

The demonstration of corresponding states for thermal conductivity follows in a manner completely paralleling the above, from the formula given, e.g., by Mori (83). We find the appropriate reduction to be

$$\kappa^* = \kappa k\epsilon^{1/2}/m^{1/2}\sigma^2$$ (V.4.16)

Strictly speaking, self-diffusion is defined only in a classical system. One may, however, regard it as mutual diffusion of a tagged species; in such a case a quantum mechanical formula similar to Equation V.4.1 may be used. Alternatively, from the start one may use the Einstein equation written in terms of a time integral of the autocorrelation of momenta for self-diffusion. The operator that replaces the similarity transform, as a formal solution of the equations of mechanics is $e^{it\mathcal{L}}$, where $\mathcal{L}$ is the self-adjoint Liouville operator (49). Using the previous reduction scheme one can easily show that the reduced classical coefficient of self-diffusion is

$$\mathfrak{D}^* = \mathfrak{D}m^{1/2}/\epsilon^{1/2}\sigma \tag{V.4.17}$$

A crude form of the theorem of corresponding states for transport phenomena has been used by Gini-Castagnoli, Pizzela & Ricci (85), and Keyes (86). These investigations deal with dimensional analysis reduction of data for liquid and solid systems, respectively. For liquids, which by the previous considerations may be expected to have transport properties obeying the simple law of corresponding states, data are available only for argon, methane, nitrogen, oxygen, and carbon monoxide. It is found that deviations from corresponding states are larger than in the case of most equilibrium properties. This may be an expression of the sensitivity of interaction cross sections to the details of the potential form, which certainly differs among monatomic, diatomic, and polyatomic molecules. Similarly, the principle of corresponding states is only approximately satisfied by the thermal conductivity of rare gas solids, presumably because of imperfection scattering and other extraneous effects. The Chapman-Enskog theory, which obeys corresponding states, closely predicts the transport properties for dilute gases. Data in the dense gas region are not sufficient for a quantitative test.

VI. SELF-DIFFUSION IN CRYSTALS

Studies of self-diffusion in crystals have interest from at least two interrelated points of view. Since the solid state can be described to first order in terms of the distribution of normal modes, it is conceivable that the mechanism of self-diffusion can be directly linked with the dynamical properties of the lattice. Were this possible, inversion of the procedure leads to the expectation that determination of the self-diffusion constant as a function of temperature, pressure, foreign solute concentration, and any other relevant parameters could be used to indirectly determine the effects of vacancies or other defects on the lattice, the role of foreign atom concentration on vacancy clusters, and so forth.

In contrast with the very considerable advances in experimental technique, the theory of crystal diffusion is still unable to explain, in fundamental terms, effects arising from changes in electron density in metallic solids, the effect of extended crystal imperfections on the diffusive trajectory, the ratio of "motional volume" to "formation volume" when point defects are present, and many other effects. To be sure, phenomenological discussions of the above have been given that probably contain the relevant physical ideas. However, the relationship of the phenomenological arguments to the fundamental lattice or electron dynamics or both is an unsolved problem in many cases.

The theory of self-diffusion has been customarily based on an application of the transition state formalism to the trajectory an atom must follow (88). To be meaningful, the formalism must ultimately justify the tacit assumption that the activated state has a sufficiently long lifetime to have meaningful thermodynamic properties. Moreover, the work required to create the

activated state is ambiguously defined since the creation of the activated state cannot be accomplished by any known processes. Finally, if the vacancy mechanism for self-diffusion is considered, the activated state theory by the use of averaged quasi-thermodynamic parameters bypasses the fundamental question of the dynamical effects of the vacancy. It has been common practice in the past to take the basic jump frequency as the Debye frequency, $k\Theta_D/h$, although there is no obvious connection between Θ_D and the diffusive process.

A different model, basically related to the activated state model, has been proposed (89) on the basis of an extension of Slater's theory of unimolecular reaction rates (90). Motion along the diffusive trajectory is due to the superposition of many normal modes, and this motion is assumed to be irreversible when the vibrational amplitude exceeds a critical distance, q_o. A diffusive jump requires the simultaneous attainment of the critical amplitude in the proper direction, and a motion of the near neighboring atoms permitting the diffusing particle to pass through to the vacant lattice site. If it is assumed that the probability of finding the shell atoms in the required configuration is given by the equilibrium probability for such an occurrence, it may be shown that (89, 91)

$$\mathfrak{D} = \gamma a^2 \nu \phi \, e^{-U_o/kT} \prod_j e^{-U_s/kT} \prod g_{k1}{}^{(2)} \tag{VI.1}$$

where the fundamental jump frequency ν is related to the normal mode frequencies ν_i by

$$\nu^2 = \frac{\sum_i \alpha_{1i}{}^2 \nu_i{}^2}{\sum_i \alpha_{1i}{}^2} \tag{VI.2}$$

and α_{1i} is the contribution (projection) of the ith normal mode along the diffusive path q_1. The energies U_i are related to the critical coordinates for central atom (q_o) and shell atoms (q_{jo}) by

$$U_o = \frac{q_o{}^2}{\sum_i \alpha_{1i}{}^2} ; \quad U_j = \frac{q_{jo}{}^2}{\sum_i \alpha_{ji}{}^2} \tag{VI.3}$$

and the pair correlation functions $g_{kl}{}^{(2)}$ may be also written entirely in terms of normal modes, i.e.,

$$g_{12}{}^{(2)} = v^{2/3} \frac{\prod_3^{3N} \left(\frac{2\pi kT}{m\omega'_\mu{}^2}\right)^{1/2}}{\prod_1^{3N} \left(\frac{2\pi kT}{m\omega_\mu{}^2}\right)^{1/2}} \exp\left[\frac{\sum \frac{L\mu^2}{m\omega'_\mu{}^2}}{2kT}\right] \exp\left[\frac{U_1 + U_2}{kT}\right]$$

$$\times \exp\left[-\frac{1}{2kT}(a_{11}q_1{}^2 + 2a_{12}q_1q_2 + a_{22}q_2{}^2)\right] \tag{VI.4}$$

$$L_\mu = \sum_3^{3N} (a_{1i}q_1 + a_{2i}q_2)R_{i\mu}$$

$$v^{2/3} = \pi\langle q^2\rangle$$

with $R_{i\mu}$ a normal eigenvector component of the modal matrix, q_i the displacement of atom i, $\langle q^2 \rangle$ the mean square thermal amplitude and ω_μ, ω_μ' the eigenfrequencies in the crystal when no atoms and when two atoms are held fixed. Equation VI.1 therefore formally represents the diffusion coefficient in terms of the normal modes of the crystal, presumed known. Such a representation would be useless unless information can be extracted from the formalism. Fortunately, extensions of the formalism as well as model calculations lead to interesting results.

It may be shown that if, instead of writing the probability of occurrence of a critical configuration in terms of pair correlation functions, it is written in terms of the force constant matrix, then the energy of activation is approximately the elastic energy associated with minimal local deformation (92). The approximations arise in the replacement of a mechanical displacement by its ensemble average, as well as in the inversion of the force constant matrix. This result provides a justification for the use of the temperature dependence of the bulk modulus to calculate the entropy of activation, a procedure first suggested by Zener.

Of more interest is the predicted temperature and pressure dependence of the diffusion coefficient (93). In most crystalline metals the activation volume for self-diffusion is of the order of one-half the molar volume. This activation volume includes both the volume of formation of the vacancy as well as the "motional volume." While it is not impossible to reconcile the observations with the simple activated state model, there is no *a priori* method of estimating the relaxation effects and other items.

In the dynamical model, we proceed by noting that the effect of an applied pressure is to shift the lattice positions of all atoms and cause an increase in potential energy. By Rayleigh's theorem, the change in the ratio of potential energy to kinetic energy leads to a corresponding change in the crystal eigenfrequencies. Since the amplitude of a given normal mode varies as ν^{-2}, in a harmonic crystal the effect of the pressure is to decrease the amplitude of vibration and keep the mean vibrational energy constant, but increase the static lattice potential. It may be shown that

$$(\nu_i^2 q_o^2)_p > (\nu_i^2 q_o^2)_{p=0} \tag{VI.5}$$

so that $\nu_i^2 q_o^2$ increases more rapidly than q_o^2 decreases. The constancy of vibrational energy follows from the relation

$$\left(\frac{\partial C_V}{\partial V} \right)_T = \gamma_G \frac{T}{V} \left(\frac{\partial C_V}{\partial T} \right)_V \tag{VI.6}$$

with γ_G the Gruneisen constant. If the anharmonicity of the potential is small, it may be shown that to first order the crystal may be treated as harmonic with an origin shifted due to the change in external parameter (T or p), which causes a change in lattice spacing. In this approximation the harmonic eigenfrequencies are regarded as functions of temperature and

pressure. For small pressures, it is clear that the shift in eigenfrequencies will be linear in the pressure difference, and this is confirmed by the detailed theory. But if the eigenfrequencies are functions of the pressure, then so are the energies U_o, U_i, the jump frequency ν and the correlation functions $g^{(2)}$. Consider the case of $U_o(p)$. We have to first order

$$U_o(p) = U_0(p = 0) + k_1 p \tag{VI.7}$$

where k_1 is known from theory, but is complicated, and difficult to calculate from first principles. Now consider a new pressure scale in which the melting temperature at pressure p, $T_m(p)$ is used to represent p. Again,

$$T_m(p) = T_m(p \approx 0) + \frac{dT_m}{dp} \, p \tag{VI.8}$$

where $p \approx 0$ indicates that the one atmosphere melting point is used and not the rigorous zero pressure limit. If we write the constant $U_o(p = 0)$ in terms of the constant $T_m(p = 0)$ and combine terms

$$U_o(p = 0) = k_2 T_m(p = 0)$$

$$U_o(p) = \left(\frac{k_1}{dT_m/dp} \right) T_m(p) + \left(k_2 - \frac{k_1}{dT_m/dp} \right) T_m(p \approx 0) \approx k_2 T_m(p)$$

since the term $(k_2 - k_1/(dT_m/dp)) T_m(p = 0)$ is negligible relative to the term retained. By proceeding to analyze the other variables in the same manner it may be shown that $\mathfrak{D}$ is a function of the one variable (T_m/T),

$$\ln \mathfrak{D} = f(T_m/T) \tag{VI.10}$$

and thereby, with the aid of the Clapeyron equation

$$\frac{\Delta H_m}{\Delta H\dagger} = \frac{\Delta V_m}{\Delta V\dagger} \tag{VI.11}$$

with the dagger indicating activation parameters.

There are two ways in which the preceding analysis can be checked (94): Is $\mathfrak{D}$ indeed a function only of T_m/T and does the relationship between fusion and activation parameters hold? The most extensive data available are for the case of Pb (94), for which $\mathfrak{D}$ is a function of T_m/T over a range of $150°$ and 8000 atm. Other substances have also been shown to follow this rule, but care must be used since the derivation requires constancy of all the elastic coefficients. This is not maintained in the case of Na, where a correction must be applied. When this is done, a universal curve of $\mathfrak{D}$ versus T_m/T is found. For the case of Pb, using the known data, the calculated heat of activation is 24,210 cal./mole and that observed is 24,300 cal./mole. For the case of Na, agreement within 5 per cent is attained when the elastic constants are corrected; and in the case of Li, agreement to within 3 per cent is attained if the value of ΔV_m is taken directly from Bridgman's measurements of melting temperature as a function of pressure. The tabulated values are averages over either 4000 or 8000 atm. increments and do not clearly show

the curvature evident in Bridgman's data. It is pertinent to comment that in reality very few data are available even for simple systems.

It is also possible to derive considerable information from simple models for which exact analytic solutions can be found for the various parameters (95). From these model studies it is suggested that:

(a) The jump frequency is insensitive to the normal mode modifications produced by the adjacent vacancy.
(b) There is considerable relaxation about a vacancy.
(c) The volume of formation of a vacancy is related to the molar volume by

$$\Delta V^* \approx \frac{V}{\gamma_G - \frac{1}{3}}$$

where γ_G is the Gruneisen constant. This result is consistent with experiment, since $\gamma_G \approx 2$ for most metals.
(d) An estimate of reasonable accuracy (25 per cent) can be made of the activation energy for self-diffusion from a knowledge of the diffuse x-ray scattering (mean square vibrational amplitudes) of the crystal.

The preceding analysis has not clarified the fundamental problem of the introduction of irreversibility. It is not clear at present whether anharmonic forces are necessary for irreversibility, although it may be shown that they are sufficient. For, if the mean time required for dispersal of the wave packet— constituted of the properly phased normal modes causing the diffusive jump —is short relative to the time between jumps, the motion is irreversible by virtue of the dilution of the normal modes into the infinite reservoir. The question of the ratio of the two times mentioned is at present unanswered. It can be shown (96) that in the presence of anharmonic forces two time scales are established, one for jumps between lattice sites and one for vibrations about a given lattice site. The calculations suggest that the dissipation of energy occurs almost entirely by relaxation of "recaptured" particles, little energy being lost in the transit across the barrier. It is also of interest that remarkable concordance exists between the structure of the preexponential factors for both quasi-equilibrium and nonequilibrium theories. The dependence of $\mathfrak{D}$ upon the coupling constant ($\alpha_{i}{}^{2}$ in the quasi-equilibrium case), the temperature, and the normal mode frequencies is the same in both cases. Only the mass dependence is different, the nonequilibrium theory of Bak & Prigogine (87) predicting $\mathfrak{D} \propto \mu^{-2}$ and the quasi-equilibrium theory predicting $\mathfrak{D} \propto \mu^{-1/2}$ with μ a reduced mass. There are at present no experimental data suitable for distinguishing between these two alternative predictions.

Allnatt & Rice (57) have studied the heat of transport for the vacancy mechanism of diffusion. The procedure consists of examining the nature of a random walk in the presence of both temperature and chemical potential gradients. By comparison of the random walk flux with the flux calculated

from irreversible thermodynamics it is shown that

$$Q_1 = \Delta H_m\dagger \qquad\qquad (VI.12)$$

where Q_1 is the heat of transport and $\Delta H_m\dagger$ the heat of activation for motion. This result is in excellent agreement with the experiments of Patrick and Lawson on vacancy diffusion in AgBr.

Of equal interest is the observation that Equation VI.12 provides a criterion of the mechanism of irreversibility. The indicated relationship is just that expected if an atom jumps into a vacancy and dissipates its energy before jumping again. The energy dissipated is clearly $\Delta H_m\dagger$ since the vacancy is already formed. But this picture implies that the energy is given up rapidly in the time between jumps and therefore that the superposition of normal modes must dissipate rapidly relative to the time between jumps. Thus it is probable that the dominant source of irreversibility in vacancy motion is the very short lifetime of the wave packet leading to the jump. We have still not established the necessary considerations for irreversibility, but the sufficiency of the conditions quoted is clearly supported by the available experimental data.

VII. CONCLUSIONS

Transport theory is at present developing rapidly enough so that any predictions of the directions the theory will take are likely to be erroneous. Nevertheless, the authors believe that five observations are pertinent.

(a) It is likely that the use of autocorrelation functions and the fluctuation dissipation theorem will provide powerful tools for the actual computation of transport coefficients, even in dense media where accurate distribution functions are needed.

(b) Approximate calculations based upon expansions along a diffusive trajectory, or some similar approximation, can be carried out to higher order than has been done herein. Extensive data are needed for simple systems so that good expansion parameters can be identified. The approximate theory does not give any "natural" expansion parameter. In the theories discussed herein, the expansion parameter was selected on an intuitive basis with very weak support from approximate analyses.

(c) Time smoothing may be regarded as a most fruitful technique of transport theory—sufficient to obtain many interesting results, but obviously not the best or most convenient technique. It is likely that the more general analyses of Van Hove, Brout, Prigogine, Balescu, Henin, etc. can be used to study media where the perturbations are strong. In a sense, what is required is a diagram technique, such as that of Mayer that permits the reordering of terms according to the strength of discontinuities. The Prigogine diagrams have many of these properties but do not seem the best form for liquid systems. No doubt if such an analysis in diagrams can be made, the new diagrams will be closely related to those of Prigogine *et al*.

(d) A complete virial expansion for the time and space evolution of the

singlet distribution function is of interest but will be useful only when terms can be summed. In this, as in the preceding three comments, an essential difficulty appears in the three-body terms. It seems probable to the authors that the theory can be cast into a form which depends upon a *restricted* three-body problem where more studies by numerical methods would probably be useful.

(*e*) In view of the preceding remark, it is likely that the theory of transport in liquids must evolve from a combination of the autocorrelation function approach and the discovery of a suitable expansion parameter and its accompanying approximate theory.

The authors hope that this presentation will prove to be a suitable introduction to a fascinating and important field of research. If this hope is fulfilled, or if any interest in further work is stimulated by this article, our aim will have been accomplished.

VIII. ACKNOWLEDGMENTS

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FUSED SALTS[1]

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INTRODUCTION

Fused salts constitute a very special class of liquids and solvents about which, unfortunately, all too little is known. Unique properties of fused salts are associated with the fact that they are usually highly dissociated into their ionic species, and, therefore, are good conductors of electric current. Indeed, they should generally be looked upon as completely dissociated and highly concentrated electrolyte solutions. Therefore, it is difficult to study the electrolytic effects associated with small changes in concentration of another species dissolved in a fused salt.

Chemical investigation of fused salts attracted much attention about 40 years ago. During the early 1920's, the work of Biltz, Jaeger, Kapma, Klemm and others of the European schools did much to lay a broad foundation for our understanding of fused salts. Early studies were especially concerned with electrical conductance, density, melting point, viscosity, and surface tension of pure salts; studies of simple mixtures were included. Much attention was given the phase diagrams as determined by freezing curves for numerous binary and tertiary systems, and numerous early studies were made of electrode potentials, particularly as they applied to the winning of active metals from their ores. In the late 1920's the study of fused salts declined and only within the past 8 or 10 years has there been a resurgence of interest. Recent work has been concerned both with the same topics studied years ago and with important questions of structure, the applications of chemical kinetics, solubility relationships, and the use of modern physical methods of investigation. A beginning has been made in the development of a statistical theory of melts.

Michael Faraday was the first to study fused salts in a systematic, scientific manner (1). He studied about 50 molten salts, obtained a comparative electromotive force series of the elements in these salts, and established the fundamental law of electrolysis that bears his name.

This review will be concerned largely with recent advances in our understanding of the structure and chemistry of fused salts. Although some references will be made to earlier work, no pretense of complete coverage is claimed. Our objective is to discuss the more recent studies and to indicate some of the unsolved problems. There are three major fields of interest in fused salts: structure, thermodynamics, and general kinetic properties that include electrical, thermal, and material transport behavior.

The resurgence of interest in fused salts can be found in their potentiality as reaction media for carrying out homogeneous liquid phase reactions

[1] The survey of literature was concluded December 31, 1959.

at elevated temperatures. It is well known that fused salts are good solvents for a wide variety of reactive substances. One application that has interested a number of workers is the possibility of using fused salts as solvents for compounds of uranium, thorium, and plutonium in fluid-fueled nuclear reactors. Very extensive research into the properties of fused salt systems for use in nuclear reactors has been carried out at the Oak Ridge National Laboratory. Much of this work is reported in publications of the Atomic Energy Commission, many of which are unclassified. The work in this area is concerned with phase diagrams, solubility, vapor pressure, electrical and thermal conductivity, viscosity, surface tension, electrode potentials, etc. A particularly interesting series of papers dealing with solutions of metals in their various molten halides has been published by Bredig (2) and his associates. The use of pyrometallurgical methods involving fused salts for the reprocessing of fuel elements has been studied extensively, both at the Oak Ridge and the Argonne National Laboratories. Also exciting spectroscopic studies of fused salts have been made at both of these laboratories.

Fused salt technologies have been used for many years in the winning of aluminum, magnesium, and certain other active metals. However, these techniques were more art than science until the recent scientific studies were made that bear directly on the mechanisms of such extractive processes. Several metallurgical laboratories in the United States, in England, in Norway, and especially in Russia are devoting considerable effort to the study of the basic properties and reactions of molten salts at quite elevated temperatures.

Little is known of the solubility and reactivity of most substances dissolved in molten salts; accordingly, it is difficult to use these solvents to carry out homogeneous synthetic chemical operations. In certain respects, our present knowledge of fused salt solutions is even less than that of 75 years ago for aqueous solutions. For example, little is known of the solubility of halides, oxides, sulfides, carbonates, and nitrates in fused sodium chloride. The best we can do is predict that their relative solubilities would be approximately in the order of their melting points, which may be grossly in error. Since it usually is impossible to predict what precipitates and gases are formed, it is unrealistic to predict what metathetical reactions may occur between substances dissolved in simple fused salts.

Acid-base theory is certainly important in considering reactions in molten salts. However, reactions that occur in aqueous systems may be very different from those that occur in fused salts, especially when hydrogen ions are involved. However, many common acid-base reactions of aqueous chemistry do occur in fused salts. For example, potassium dichromate dissolved in fused sodium nitrate gives the characteristic color of the dichromate ion. The addition to this solution of a little solid sodium carbonate promptly causes an acid-base reaction in which carbon dioxide effervesces from the solution and its color changes to that of the chromate ion, according to the equation:

$$Cr_2O_7^- + CO_3^- = 2CrO_4^- + CO_2.$$

Many oxidation-reduction reactions do not occur in aqueous systems without the presence of an appropriate concentration of hydrogen ion and water is a product of the reaction. In fused salt solutions, oxidation-reduction reactions frequently take place, even though hydrogen ion is absent, because the oxide ion tends to be stable in molten salts. An illustration of this situation is the oxidation of bromide ion by bromate ion. This reaction will not occur in aqueous systems until acid is added. The reaction then is:

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O.$$
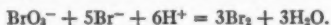
However, if bromide ion is dissolved in molten sodium nitrate, and a trace of sodium bromate is then added, bromine is promptly formed according to the equation:

$$BrO_3^- + 5Br^- = 3Br_2 + 3O^-.$$

Although a few such reactions have been studied in moderate detail (3), our knowledge of such reactions is very limited.

REVIEWS

The increasing interest in the physical chemistry of fused salts is demonstrated by the number of review articles concerning them. In recent years several important symposia have been devoted exclusively to molten salts or molten silicates. One of the first considered molten slags and salts and was held by the Nuffield Research Group in Extractive Metallurgy in London, 1952. The proceedings of this symposium have been published under the title *Physical Chemistry of Melts* (4). Because of interest in fused salts in nuclear reactor technology, the Oak Ridge National Laboratory was host to fused salt conferences in 1956 and 1957. The American Chemical Society held a symposium on fused salts in Miami in 1957, and in 1959 numerous papers on fused salts were presented at its Symposium on High Temperatures. A substantial section of the Symposium, *High Temperature—A Tool for the Future*, Berkeley, California, June 25–27, 1956 (5), was devoted to the behavior of molten salts. Janz, Solomons & Gardner (6) have published a review on the physical properties and constitution of molten salts with particular reference to electrical conductance, transport, and cryoscopy. A recent summary article on the electrochemistry of molten salts was by Bloom & Bockris (7). These authors discussed structure, methods of study, and properties, and also included a discussion of molten oxide systems. An interesting paper by Watelle-Marion (8) discusses conditions that must be known in order to define the structure of a molten salt: whether the liquid is composed of simple ions, molecules, or complexes; the nature of the forces that exist between the several entities of the solution, including the degree of dissociation; and some sort of a reasonable distribution function to represent the properties of the liquid. Petit (9) has written a review on cryoscopy at high temperatures, in which the techniques, results, and interpretations

of the measurement of freezing point depression in fused salts, especially cryolite, are discussed.

An important question concerning molten salts deals with the existence and structure of complexes. Antipin (10) reviews this subject through 1953. This general problem has since been discussed by Van Artsdalen (11, 12).

A brief report by Nachtrieb (13) deals with the analytical chemistry of fused media.

Considerable work on the chemistry of molten salts has been reported by Russian authors. Much of it, however, is concerned with phase equilibria and is outside the scope of this review. Delimarskii (14, 15) has published reviews on the work of the Institute of General and Inorganic Chemistry in Kiev through 1953, and has also published a review on electrode potentials in molten salts covering research through 1956. The Russians have recently organized an Institute of Electrochemistry (16) that will be primarily concerned with the study of fused salts, including the mechanism and kinetics of electrode processes of the boundary between metals and semiconductors. Lushnaya, Evseeva & Vereshchetina (17) have considered the physical properties of salt melts, especially those containing nitrates, and the nature of their structural parts.

TRANSPORT PROPERTIES

Viscosity

The determination of viscosity constituted much of the work on fused salts in the 1920's. It is not intended in this review to consider this work, however, one or two of the early papers that are more or less classics should be mentioned. Goodwin & Mailey (18, 19), in a series of papers in 1908 on the density, electrical conductivity, and viscosity of molten salts, were probably the first to lay a sound comparative foundation. They studied a series of molten nitrates and attempted to uncover whatever relationship might exist between electrical conductance and viscosity. They concluded that the ionic dissociation of the fused salts that they studied did not change with temperature, and that the fluidity of mixtures was not an additive property. Lorenz (20, 21) published some of the best early work on the viscosity of molten alkali metal salts and molten silver halides. In 1928 Dantuma (22) published a very detailed study of the viscosity of molten alkali nitrates and chlorides. He obtained a cubic power equation for the dependence of viscosity on temperature over fairly wide temperature ranges.

Karpachev and his associates (24, 25, 26) published several papers in the mid-1930's dealing with the viscosity of various molten salts and mixtures. Mixtures such as $KCl-MgCl_2$ (25) had sharp peaks in the viscosity versus composition isotherms; they interpreted this as indicating the presence of complexes. It is certainly reasonable to expect that if large complexes are formed in a molten salt, these will not flow with the ease of smaller ions; therefore, one might expect an increase in viscosity in systems in which complexes exist. More recent studies by Harrap et al. (27, 28, 29) have con-

sidered this problem in greater detail, including its relationship to molar volume and electrical conductivity. These studies appear to be among our most accurate investigations of viscosity in molten salts. Harrap & Heymann (28, 29) have correlated temperature effects with rate theory for both pure salts and mixtures, and have considered the electrical conductivity and viscosity in the systems: AgCl-AgBr, PbCl$_2$-PbBr$_2$, AgCl-PbCl$_2$, AgCl-KCl, and AgBr-KBr. None of these systems shows compound formation in the solid state; when fused they show deviations from simple additivity in electrical conductance that varies with the size and charge of the replacing ion, and their viscosity isotherms are similar to those for ideal binary, nonpolar, liquid systems. Pugsley & Wetmore (30) have studied the viscosity of fused silver nitrate and have shown that Frenkel's relation for comparing the temperature dependence of viscosity and conductivity is valid for this system, and that the energy of activation for viscous flow is proportional to that for electrical transport over a substantial range of temperature. Mackenzie (31) has described apparatus for the simultaneous measurement of density, viscosity, and electrical conductivity. It seems unlikely, however, that this method will be accurate for either conductivity or viscosity determinations. Greenwood & Wade (32) have determined a number of properties of molten gallium trichloride in both the stable and the supercooled condition. The log η vs. $1/T$ curve shows a small discontinuity near the melting point, despite the symmetrical and nonpolar nature of the gallium trichloride dimer. Actually gallium trichloride is not a typical fused salt since it apparently is not ionized, but rather is in molecular form including dimeric molecules.

ELECTRICAL CONDUCTIVITY

The most striking characteristic of fused salts is their high electrical conductivity. Mostly, they are Faraday-type conductors in which individual ions carry the charge. However, it has been shown by Derge *et al.* (33 to 37) that certain molten sulfides and selenides behave as electronic semiconductors, with p and n type characteristics depending on the nature of the nonstoichiometry of the system.

Among the earliest theoretical studies of the electrical conductance of molten salts are those of Frenkel (23, 38). He derived mathematical equations for the relationship of viscosity and electrical conductance, basing his interpretations on the earlier work of Biltz, Jaeger, Kapma, Klemm, and others. In the case of alkali and alkaline earth halides, they had established that for any particular cation the conductance did not change greatly with change of anion, but the viscosity increased rapidly as the size of the anion increased. They had also shown, for the same halides, that the electrical conductance decreases markedly and rather regularly as one goes down the series from lithium to sodium to potassium to cesium with any given halogen anion. Frenkel proposed that the small cation was largely responsible for determining electrical conductance. On the other hand Frenkel suggested

that viscosity depended primarily upon the anion. Assuming essentially complete ionization of the salts, Frenkel devised equations for simple mixtures, such as AgCl-AgBr, in which he obtained mathematical relationships between conductance and viscosity in terms of the concentrations of ions and the logarithms of their activity coefficients.

More recently, Oldekop (39) has used Born and Green's statistical theory in calculating the electrical conductance and the viscosity of molten alkali halides. His results, however, have been criticized by Janz *et al.* (6).

Electrical conductivity in molten salts has generally been measured by methods similar to those used in aqueous and semiaqueous systems. Sometimes minor difficulties are introduced because of the corrosive nature of the high temperature melts and their tendency to abstract impurities from either the container or the conductivity cell. The electrode material has usually been platinum, frequently covered with a so-called platinum-gray (40), which results when platinum-black is heated in the melt. Most investigators use some form of capillary cell for measurements in highly conducting molten salts. Generally the cell has been calibrated at room temperature with aqueous potassium chloride solution of accurately known conductivity. Standard bridge techniques are generally employed. Occasionally, however, for highly corrosive systems such as fluorides, four-probe devices are used in conjunction with a regular or modified Kelvin bridge, such as that of Yaffe & Van Artsdalen (41).

Polarization phenomena are such that it is desirable to measure the resistance over a wide range of frequency and extrapolate to a value at infinite frequency. However, for fused salts the correction rarely exceeds 1 or 2 per cent. Kröger & Weisgerber (42) have observed the polarization resistance on bright platinum electrodes as a function of A.C. frequency in molten nitrates; in agreement with others, they found that the polarization resistance is proportional to $1/\sqrt{w}$. Unfortunately, numerous otherwise satisfactory determinations of electrical conductance have been marred by a failure to measure the density of the liquid salt. Such measurement is necessary to compute its molar volume, which is used in converting specific conductance to equivalent or molar conductance.

The more recent studies of electrical conductance have generally treated the phenomenon as a typical rate process and have applied the usual rate equations to determine an activation energy for electrical migration of the appropriate ions. Early workers tended to relate the specific conductivity to a linear equation in temperature. More exact recent determinations of the temperature dependence of conductance have shown, however, that it is generally quadratic in temperature dependence. A plot of the logarithm of the equivalent conductance against the reciprocal of temperature usually results in an almost straight line, thus showing that the activation energy for electrical migration is approximately constant with variation of temperature. However, Yaffe & Van Artsdalen (43) have shown that even for simple salts there is frequently a small deviation from linearity in the plot and,

hence, that activation energy is slightly dependent on temperature. This dependence may be either positive or negative, hence subject to the peculiarities of the individual melts. The rate equation for electrical conductance can be expanded in the usual way to include both an entropy and an enthalpy of activation. One of the terms required to calculate entropy of activation exactly is the microscopic dielectric constant. No values for this constant are available for fused salts, so reasonable values must be assumed (fortunately the result is not greatly influenced by this choice). Nonetheless, it is found that the entropy of activation is negative and generally about 7 to 10 entropy units (40, 44). The indicated sign and magnitude of the entropy of activation are reasonable for a process that involves the slipping of one ion past another. This seems to argue that the conduction process is similar in all of the cases studied.

Yaffe & Van Artsdalen (41) have reported the electrical conductivity of some Group II halides and of several selected rare earth halides. It can be concluded from their work that Group I and Group II halides in the fused state have equivalent conductances that are comparable with their equivalent conductances in infinitely dilute aqueous solution at room temperature. On the other hand, the rare earth halides had equivalent conductances in the melt that were about one-tenth to one-twentieth of their values in infinitely dilute aqueous solution (where they are known to be "strong" electrolytes). Yaffe and Van Artsdalen suggest that this indicates the rare earth halides they studied to be somewhat self-complexed in the melt.

Determination of the conductances of molten fluorides has generally been complicated by their highly corrosive nature. Yim & Feinleib (45) reported values for several Group I fluorides and Yaffe & Van Artsdalen (41) measured three molten alkali fluorides. Their work is in satisfactory agreement.

Most recent work on the electrical conductance of fused salts has been aimed more at the study of mixtures than individual pure components, although the pure components for systems under investigation have usually been measured with care. One of the underlying reasons for the interest in mixtures has to do with determining whether complexes exist. One would anticipate that if large complexes are formed, their electrical mobility would be reduced below that of small ions and, therefore, electrical conductance should decrease. Bloom & Heymann (46) observed that the activation energy for conduction is greater for multivalent than for monovalent ions, and suggested that an increasing amount of "covalency" tends to decrease energy of activation. In none of the systems that they studied did they observe that molar or equivalent conductance was a linear function of mole fraction. They conclude that fused salt systems showing no evidence for complex ion formation usually tend to exhibit moderate negative deviations from additivity of electrical conductance. Studies by Van Artsdalen & Yaffe (40, 43) showed similar behavior for chlorides and iodides of Group I elements. These authors point out the danger of attempting to ascribe deviations from additivity to a formation of complex ions. They observed sub-

stantial negative deviations from additivity and in the case of the LiCl-KCl system actually found that at 80 mole per cent KCl the conductivity was less than that of pure KCl despite the fact that pure LiCl is a far better conductor than KCl. Their studies show that for a given anion the negative deviation from additivity for those systems not forming complex ions is greater for cations having the larger difference in size. This may also be stated in the following way: Negative deviations from additivity in binary mixtures increase as the difference in conductivity of the pure components increases. Bloom *et al.* (47) studied a number of different mixed salt systems such as nitrate-nitrite systems, chloride-iodide systems, etc., in some of which the anion was varied while in others the cation was varied. They concluded that those systems that do not show compound formation in the solid phase tend to show only moderate deviations from additivity of equivalent conductance in the liquid phase. On the other hand, considerable deviations from ideal additive behavior were found for those systems in which the phase diagrams indicate the presence of solid compounds. They interpret this to mean that such mixtures are considerably more covalent than the pure salts. In this sense, covalent apparently means the formation of coordination complexes.

Russian workers, as well as others, have published extensively on various systems involving aluminum halides with alkali and alkaline earth halides. It has been shown that adding sodium chloride or bromide to the poorly conducting (molecular) aluminum chloride or aluminum bromide greatly increases the electrical conductance. This is interepreted to mean that a complex halide of aluminum is formed which is an anion in the melt. Studies of alkali halides and zirconium tetrachloride have been made by Howell & Kellogg (48); they showed that zirconium forms complex chloroanions as evidenced by the substantial increase in conductivity of the mixtures over the pure zirconium tetrachloride. Another somewhat "covalent" compound, beryllium chloride, has been studied in various molten salt solutions, and here, too, it has been shown that complex anions are formed. The addition of sodium chloride to molten beryllium chloride vastly increases its conductivity, indicating the formation of chloroberyllium anions. Delimarskii and associates (49) have attempted to use their determinations to calculate the degree of electrical dissociation of molten $BeCl_2$.

Hill & Wetmore (50) studied the electrical conductance of the system $AgCl$-$AgNO_3$ and tied it in with measurements of transport fractions to show that AgCl in dilute solutions of $AgNO_3$ may be regarded as being almost completely in the form of a complex ion Ag_2Cl^+. The mobility of this complex was shown to be about half that of Ag^+.

In a series of interesting papers, Sakai (51 to 55) has considered the electrical conductivity of simple and mixed salts. He has discussed the formation of possible complexes and their effect on conductance. His studies of mixed systems have been concerned mainly with various halides in which

one might anticipate the formation of complexes, as for instance with cadmium, lead, magnesium, etc.

Fewer studies have been made of mixed systems in which one would not anticipate the formation of strong complexes. Van Artsdalen & Yaffe (40) studied the systems LiCl-KCl, NaCl-KCl, and KCl-KBr. Story & Clark (56) investigated the system $NaCl-CaCl_2$ and described the use of a modified Kelvin bridge in making the measurements with a capillary type four-lead fused quartz dip cell. Cowen & Axon (57) measured electrical conductivity of the fused binary systems $AgNO_3-KNO_3$ and $AgNO_3-LiNO_3$ but unfortunately did not determine density, so their data are reported as specific conductance only. They show that the activation energy for these systems varies with temperature, as was observed in halides by Van Artsdalen & Yaffe (40). The $AgNO_3-NaNO_3$ system was studied by Wetmore and associates (58). They determined that the activation energy for migration decreases with rising temperature, which they also found to be true for pure silver nitrate. Protsenko (59) determined electrical conductivity of the mixed nitrate systems of lithium-rubidium and silver-rubidium in a molten state. His measurements of conductivity did not indicate the existence of congruent melting compounds. The conductivity isotherms increased smoothly from the less conductive to the more conductive component with a modest negative deviation from additivity.

The theory of conductivity of fused salts has been discussed in terms of relatively low melting substances such as the nitrates and halides of alkali metals. Recently a series of studies on molten oxides was made by Van Arkel, Flood & Bright (60). These measurements, which must be made at relatively high temperatures, are more difficult than those made below 1000° with halides or nitrates and, therefore, are somewhat less accurate. These authors, however, were able to obtain reasonably good conductivity data for a substantial number of oxides of elements chosen from various sections of the periodic table. Their results confirm the conclusions about bonding type and structure of fused salts that had already been obtained with lower melting salts.

It has already been noted that many fused sulfides are quite different in that they show electronic conduction and act as electronic semiconductors. However, the situation is not quite this simple. The studies show that both types of conductance, electronic and ionic, are significant contributors to the overall conductivity. It seems likely that other molten compounds, which are not stoichiometric, will be found to exhibit electronic conduction similar to that found in solid semiconductors.

Many studies have been made of the electrical conductance of a host of different molten silicates, which, of course, are of great technical importance in winning metals from their ores. Systems important in electrowinning of aluminum have been studied more than some others. In an important recent investigation, Edwards et al. (61) made measurements of systems of fluorides

in a region of interest to the aluminum industry. More recently Foster and his associates have extended this work in cryolite and NaF-AlF$_3$ melts with the objective of determining the mechanism of conductance and correlating transport processes with constitution. Foster (62, 63) attempted to obtain transport numbers for various postulated complex ions containing fluorine. He concludes that many compounds are incompletely dissociated in the cryolite melt and that the conductance is largely by sodium ion. This seems reasonable in view of the near certainty that the fluoride ion is highly complexed with aluminum to form an anion. Several Norwegian investigators have also investigated molten cryolite-aluminum oxide systems (64).

Several fine studies of conductance and other properties of molten silicates have been made by Bockris and his students (44). They determined transport numbers and conductance in a number of molten silicates. Bockris & Mellors (65) measured conductance over a wide temperature range for systems of lead silicates and lead borates. Baak (66) has made a careful study of the validity of Faraday's laws in systems of silica with FeO and CoO in proportions that correspond fairly well with that of known silicates. He reports that cobalt silicates exhibit cation conductance if the basicity is below a certain value; and semiconductance otherwise. He has obtained relations between conductivity and composition and states that ionic mobility is inversely proportional to the square of the ionic radius.

The nature of solutions of metals in various molten salts has been an intriguing problem for many years. One of the earliest papers concerning the electrical conductivity of alkali salt melts containing a stoichiometric excess of alkali metal was by Mollwo (67). Since most molten metals are vastly better conductors than molten salts, it follows that, at a sufficiently high concentration of metal, electrical conductance must increase drastically. Mollwo considered that the alkali metals exist in their halide salts as free atoms without yielding electrons. More recently the properties of metal-metal salt solutions have been extensively studied from a variety of angles by Bredig and his associates at the Oak Ridge National Laboratory. Bronstein & Bredig (68) measured the electrical conductivity of alkali metal solutions in their molten halides. They report that the equivalent conductance of potassium in KCl and KBr increases with increasing metal concentration, but for sodium in NaBr it minimizes at about 9 mole per cent metal. They suggest that the different behavior of sodium and potassium may be related to the liquid phase equilibria and the dissociation energies for diatomic gaseous metal molecules. At the temperatures in question, sodium shows a greater tendency to dimerize than does potassium. Mellors & Senderoff (69) have studied the system Ce-CeCl$_3$. They conclude that oxidation states of cerium lower than Ce^{3+} are formed, and the remaining Ce^{3+} is complexed, probably to form $CeCl_4^-$. They propose that dissolved metallic cerium dissociates to produce Ce^{1+} plus electrons and that these comparatively free electrons become trapped in the molten salt. Thus, conductance is partially ionic and partially electronic.

It is obvious that the study of metal-metal salt solutions is an important field and much additional work remains to be done in order that their exact nature may be elucidated.

TRANSPORT NUMBERS

Transport numbers of the conductive species in electrolytic solutions are important quantities. Various experimental procedures have been used by different investigators to determine transport numbers in fused salts. Unfortunately, there is a difficulty in applying the usual definition of transport number to a simple, single, fused salt that results from the lack of a suitable frame of reference, as engendered by the requirement of electroneutrality. Any transport number obtained can depend upon the way in which it has been determined. Schwarz (70) long ago pointed out this difficulty. More recently this problem has been discussed by Van Artsdalen (11, 71), Sundheim (72), and Laity (73). Fortunately, this problem exists neither for mixtures of salts nor for a single pure compound that can be viewed as composed of two simpler compounds, e.g., $K_2ZrF_6(2KF+ZrF_4)$.

Recent studies of the applicability of several experimental techniques to the determination of transport numbers of individual ions in a single pure fused salt have been made by Duke and his associates. Duke & Laity (74, 75) used a bubble-cell type apparatus in which a fine porous membrane separated two arms of the liquid and a bubble in a capillary between the two arms was used to determine the actual transport of liquid by the electric current through the membrane. They found a transport number of about 0.75 for chloride ion in molten lead chloride. Duke & Fleming (76) described a technique employing a radioactive tracer, and Duke & Cook (77, 78) described a modified Hittorf method. They also listed results obtained by their modified moving boundary method that agreed with the prior studies of Duke and Laity on lead chloride. Duke & Owens (79) reported transport numbers for the fused salts $LiNO_3$, $NaNO_3$, KNO_3, and $AgNO_3$. Their results indicate that the transport number decreases with increasing cation size. Similarly, Duke & Bowman (80) report that the transport numbers of chloride ion in a series of Group I chlorides increase with cation size. Duke's results show reasonable agreement with a calculation of transport number based on an equation due to Mulcahy & Heymann (81),

$$t_a = \frac{r_c}{r_a + r_c}$$

where t is the transport number, r the radius of the ion and the subscripts a and c refer to anion and cation respectively. Since $t_a + t_c = 1$, it follows that

$$t_c = \frac{r_a}{r_a + r_c}.$$

Bloom & Doull (82) point out that in many determinations of transport numbers, the gravitational flow of the melt in the reverse direction to that produced by the flow of electricity has introduced large errors that have

never been completely overcome by the insertion of narrow tubes or sintered disks between the anode and cathode compartments. They attempted to eliminate this gravitational flow by carrying out transport measurements in a capillary tube containing liquid electrodes at each end and leveled in such a way as to eliminate the effect of gravity. For chloride ion in molten lead chloride they obtained a transport number of about 0.4, while Duke & Laity (75), by usual procedures, obtained the value 0.75. The transport number of chloride ion in cadmium chloride was determined by Bloom & Doull to be about 0.34, and they conclude that the assumption of Duke and Laity, that such electrolytes are predominantly anion conductors, is unfounded. This work has been extended by Bloom & James (83) to pure molten silver nitrate, where they find a transport number (0.25) for nitrate ion in agreement with that found by Laity & Duke (84).

The type of membrane used in Hittorf-type transference measurements can be very important. It is desirable that the leakage rate under small hydrostatic head should be as low as possible, while the electrical conductivity should be high. Unfortunately, these requirements tend to be mutually exclusive. Lorenz & Janz (85) have studied this problem for a number of salts and different membranes. They believe that Poisseuille's equation may be used to calculate the hydrostatic head necessary to overcome friction, and suggest that transference measurements involving the movement of a gas bubble in a capillary arm may be open to serious error if a substantial hydrostatic head is required to start the bubble moving. Their experiments indicate that with salts such as molten AgCl the bubble continues to move once it is started. The problem is less severe in PbCl$_2$. They conclude that Duke & Laity (75) made sufficient allowance for this effect, hence their results are substantially correct. Lorenz & Janz point out that most molten metals have a great tendency to stick to glass and quartz and question the reliability of the method used by Bloom & Doull (82) although they believe that the principle of the method is sound. Harrington & Sundheim (86) reported observations on typical membranes used for measuring transference numbers in molten salts. They found that all membranes, except those with extremely high electrical resistance, leak with as little as one centimeter hydrostatic head of the fused salt.

The interpretation of transference number measurements in mixed salt systems is straightforward. Sundheim (87) has given a simple theoretical treatment of the coupling between diffusion and electrical conductance for a solution of two molten salts having one ion in common. The quantities of transport are said to be related to transference numbers, diffusion potential, and the steady state in the electrolysis. In recent years several papers on transference numbers in simple mixed salts have used rather straightforward interpretations. Aziz & Wetmore (88) determined relative transport fractions in molten mixtures of NaNO$_3$ and AgNO$_3$ and, surprisingly, their results indicated that transport by silver ion was greater than that by sodium ion. Duke & Owens (89) determined the mobilities of the three ions in fused

KNO$_3$-AgNO$_3$ mixtures as a function of composition. They report that the mobility of the nitrate ion is relatively insensitive to composition change and the mobilities of the cations tend toward the mobility of the main constituent ion at each end of the composition scale. The transport numbers were not affected significantly by temperature changes. Duke & Fleming (76) carried out a similar study in the fused system KCl-PbCl$_2$. The authors state that for each mixture the transport number of the chloride ion deviated positively from linearity when plotted against the equivalent fraction, while the transport numbers of the cations deviated negatively. They propose that the initial decrease in conductivity, as lead chloride is added to potassium chloride, results from depression of the conduction of K$^+$ rather than the formation of a chlorolead complex. Malkin, Khokhlov & Shvartsman (90) have used radioactive isotopes to determine the relative mobility of cations in molten oxide mixtures containing P$_2$O$_5$, Al$_2$O$_3$, SiO$_2$, CaO, Na$_2$O, etc. They determined that the cations carry most of the current, hence in sodium calcium silicate the Na$^+$ mobility is substantially higher than that of Ca^{++}. In the CaO$\cdot$Al$_2$O$_3\cdot$SiO$_2$ system the calcium transference number decreases with increasing amounts of Al$_2$O$_3$, which indicates that such melts contain aluminum in cation form.

Much interest in transference numbers and electrolytic migration has centered around fused salt electrolytic methods for the separation of stable isotopes, notably by Klemm in Germany and Lundén in Sweden (91 to 96). These men and their schools have effected substantial enrichment of isotopes by fairly simple techniques, including counter-current migration techniques.

DIFFUSION

The diffusional characteristics of the ions of molten salts are intimately connected with their transport properties, hence we may anticipate that a detailed knowledge of the diffusion processes will contribute substantially toward a better understanding of their structure. Few such studies have been made, presumably because of the difficult experimental techniques necessary for measuring diffusion at elevated temperatures. Several papers have recently appeared that examine by appropriate tracer techniques the self-diffusion of individual ions of single fused salts. The first of these was by Berne & Klemm (97), who investigated the self-diffusion of the thallous ion in molten thallous chloride. Van Artsdalen et al. (98) reported their determinations of the self-diffusion coefficients of both NO$_3^-$ and Na$^+$ in molten sodium nitrate. Borucka et al. (99) reported studies involving the self-diffusion of Na$^+$ and Cl$^-$ in molten sodium chloride. The technique used was that devised by Anderson & Saddington (100) for their classic study of self-diffusion of aqueous electrolytes.

The studies with sodium nitrate (98) and with sodium chloride (99) both showed that one cannot use the simple Nernst-Einstein equation to calculate electrical conductivity from the sum of the two self-diffusion coefficients. This equation gives substantially greater conductances than those de-

termined experimentally. Bockris and associates concluded that this dif-
ference can be ascribed to the diffusion of undissociated molecules or of
paired vacancies. Van Artsdalen (71), on the other hand, inclines to the idea
that the Nernst-Einstein equation is not applicable to fused salts because
the mechanism of electrical conductance and self-diffusion is different than
in aqueous solutions where the ions of opposite sign are not in immediate
contact. In a paper on the application of irreversible thermodynamics to
liquids, Laity (73) has pointed out that the calculation of the so-called "true"
self-diffusion coefficients by Bockris is subject to substantial imprecision
since no account is taken of the relative concentration of ions and molecules.
A very recent paper by Dworkin, Escue & Van Artsdalen (101) reports self-
diffusion coefficients for both anion and cation in a series of alkali nitrates
and silver nitrate. These authors have applied the absolute rate theory as
well as phenomenological concepts of irreversible thermodynamics as dis-
cussed by Laity (73). They show that, in general, the activation energy for
the migration of cation and anion in each of these salts is about the same
and the activation energy increases somewhat with increasing cation size.
Frictional coefficients for the nitrates, calculated by the method of Laity,
are all positive; according to Laity, this tends to indicate that a high degree
of association in the melt need not be postulated. Hence the choice of in-
dividual ions as the mobile species in the melts is probably correct. Dworkin,
Escue and Van Artsdalen also conclude that the migrations of anion and
cation are complementary interactions, although in the case of lithium ni-
trate anion-anion interaction is more important than anion-cation interac-
tion, apparently because of the great disparity in size of the ions. Self-
diffusion coefficients in these salts appear to be related to ionic radii.

The apparent activation energy for the self-diffusion of ions in molten
sodium chloride, thallous chloride, alkali nitrates and silver nitrate all ap-
pear to be in the range of roughly 4000 to 8000 cal./mole. These are reason-
able values for the heats of activation of self-diffusion. The fact that all are
of about the same magnitude indicates the near equivalence of the poten-
tials acting between the ions in a melt to restrict their migration. Wallin &
Lundén (102) have measured the self-diffusion coefficient of zinc ion in
molten zinc bromide between 400 and 640°C. They find that the activation
energy for self-diffusion of the zinc ion is 16,060 cal./mole. It is interesting
that the activation energy in this case is substantially higher than in other
salts that have been studied. This may be connected with the considerable
tendency shown by zinc bromide to form complex ions, in contrast to the
other salts for which self-diffusion has been measured.

The magnitude of the self-diffusion coefficients of the several ions present
in fused salts seems to lie in a range of 1 to 5×10^{-5} cm.^{2}/sec. Thus $\mathfrak{D}$ in
fused salts is approximately the same as for the corresponding salts in aque-
ous solution at room temperature. Likewise, it is of about the same magni-
tude as that for the diffusion of the rare gases in liquid form and is only
slightly smaller than the self-diffusion coefficients of molten metals, e.g.,

iron, at temperatures up to 1500°C. An explanation for this similarity may perhaps be found in the fact that all measurements of self-diffusion have been made in relatively narrow temperature ranges, a few to several hundred degrees above the melting points. Considering that the melting points of substances represent a sort of corresponding temperature or state, one sees that these self-diffusion measurements are made at roughly corresponding temperatures even though the actual temperatures may differ widely.

Yang & Simnad (103) have measured the rate of diffusion and electric migration of radioactive ions formed by the electrolytic dissolution of a radioactive metal anode. Such a method is susceptible to a substantial error resulting from convective currents. Angell & Bockris (104, 105) have devised a technique for the measurement of the interdiffusion coefficients of one molten salt into another wherein the two columns of molten salt to be interdiffused are initially separated by a gas bubble at reduced pressure. By applying external pressure the bubble collapses, the two liquids are brought into contact, and interdiffusion commences. The method was used on equimolar mixtures of cadmium chloride and potassium chloride; from the data the self-diffusion coefficient of cadmium was determined.

It seems likely that important information about both normal diffusion and self-diffusion of ions in molten salts will soon be obtained by a variety of techniques. The use of modern methods to study electrode kinetics should be applicable to determining diffusion and other transport phenomena in and around electrodes. It would be of interest to measure self-diffusion coefficients of as many ions as possible in mixtures for which transference numbers have been determined.

THERMAL CONDUCTIVITY

Thermal conductivity of fused salts is an important subject about which little is known. Fused salts are potentially good heat transfer media and to some extent have been used as such. Likewise, the use of nitrate-nitrite heat treating baths is well established in the metallurgical industry. Despite this, almost no careful determinations of thermal conductivity of either simple or mixed fused salts are reported. A few pioneering studies have been made at the Oak Ridge National Laboratory and are reported in various AEC documents. A recent paper by Gambill (106), based on earlier work at the Oak Ridge National Laboratory, presents a generalized estimation method for obtaining thermal conductivity data. Nagaura & Sasaki (107) have determined thermal diffusion in the fused salt system of silver nitrate-potassium nitrate. They report that silver nitrate concentrates in the region of lower temperature and have estimated the Soret coefficient to be of the order of 10^{-3}. It apparently decreases with increased concentration of silver nitrate. The thermal conductivity in fused salts appears to be higher than predicted by solid state theory. This may indicate that internal heat transfer by radiation is important in thermal conductance in transparent fused salts.

ELECTRODE PROCESSES

Two general papers should be mentioned in connection with the techniques for the study of electrode processes. The first is by Laitinen, Ferguson & Osteryoung (108), and describes the exquisite care necessary in preparing an ultra-pure fused eutectic solvent of lithium chloride and potassium chloride for studies of the mechanisms and kinetics of electrode processes. The second paper, by Hills, Inman & Young (109), is on techniques for studying electrode processes in fused salts below 1000°C.

The decomposition potentials of substances dissolved in molten salts are important quantities, not only for the understanding of electrode processes, but for the study of thermodynamics and kinetics of reactions. Unfortunately, many of the data on decomposition potentials are rather scattered and usually refer to solutions and materials of technological interest. Delimarskii *et al.* (110) obtained by polarographic methods the decomposition potentials for various metallic chlorides dissolved in fused $NaCl$-$AlCl_3$. Delimarskii (111) also described the use of graphite electrodes and graphite crucibles to obtain the decomposition potentials of a series of molten fluorides. He reports that polarization was considerably decreased below that of prior work and the anode effect eliminated. The electrochemical series of the fluorides at 1000° was $Ba > Sr > Ca > Na > K > Mg > Li$; the decomposition potentials are apparently related to ionic radius. The decomposition potentials of fused lead and thorium chloride have been determined by Smirnov & Ivanovskii (112). Sheiko & Feshchenko (113) have investigated decomposition voltage in the system K_2ZrF_6-$NaCl$-KCl. Laitinen & Liu (114) have studied many different salts dissolved in the LiCl-KCl eutectic mixture and have obtained a reasonably extensive table of electromotive force values.

The study of electrode kinetics in fused salts bids to become an exceedingly important tool in understanding their reactions and structure. Under appropriate conditions it can also give useful information about diffusion potentials and diffusion coefficients. An early paper on the kinetics of fast electrode reactions by Talvaldis & Delahay (115) mentions applications to fused salts. Laitinen & Osteryoung (116) reported impedance measurements at solid microelectrodes in molten LiCl-KCl eutectic. They considered their results in the light of a theoretical interpretation of pseudocapacity. Laitinen & Ferguson (117) developed a chronopotentiometric method of analysis for use in fused LiCl-KCl eutectic; the method is applicable to other melts (118). Laitinen & Gaur (119) reported careful and extensive impedance and polarization measurements of a variety of salts dissolved in fused LiCl-KCl eutectic. They found that most metal ions showed a tendency for "predeposition." By means of an empirical correction, they obtained normal Faradaic admittance which was used to calculate rate constants for the deposition process. Current-potential curves showing the polarization behavior in the vicinity of equilibrium potential were described and values of the transfer coefficient of the cathodic process, as well as the exchange current,

were computed by a curve fitting method. However, these calculated values of the exchange current were much lower than those obtained from impedance measurements. Further studies have been made of exchange currents in this melt and are reported by Laitinen, Tischer & Roe (120).

Delimarskii (121) has reviewed the work on polarography of molten salts through 1953. Laitinen, Liu & Ferguson (122) have discussed in some detail the polarography of metal ions in fused LiCl-KCl eutectic. They used a platinum reference electrode and a second microelectrode of platinum, tungsten, or carbon to obtain polarographic characteristics for Cd, Bi, Cr, Cu, Zn, Tl, In, Pb, Sn, Ga, Hg, and Al as chlorides. They conclude that, under suitable conditions, voltametric measurements can be used quite satisfactorily for analytical purposes. It seems reasonable to anticipate substantial advances in this area in the near future.

Several interesting studies using liquid metal electrodes have been made of polarographic techniques. Izbekov (123) has studied the electrolysis of various metal halide solutions using a number of liquid metals as electrodes (e.g., liquid tin or bismuth). Randles & White (124) have investigated the electrochemical discharge at liquid mercury electrodes of nickel and several other ions when dissolved in various fused alkali metal salts. By and large, however, polarography in fused salts has been done using solid microelectrodes.

Flengas (125) has investigated the behavior of a dipping platinum microelectrode in silver nitrate dissolved in molten sodium nitrate-potassium nitrate, and obtained solubility products that agreed well with his electrometric titration techniques (126). Three Japanese workers (127) have used vertically vibrating platinum microcathodes to study polarographic waves of zinc chloride in molten Na_3AlF_6-CaF_2. Piontelli and associates (128 to 131) have made numerous measurements of polarization voltages in molten electrolytes. They have described experimental arrangements and given results of passivity measurements.

Russian workers (132 to 134) have recently used polarographic techniques to study fused salts. They obtained typical polarographic waves, estimated the decomposition potentials and determined some interesting properties relative to the diffusional properties of electrolytes in molten salts. Some interesting automated equipment has been used in much of this work. Antipin and associates (135) described the use of a polarograph for the automatic recording of polarization curves in fused salts and concluded that the commutator method is superior to the direct compensation method. Smirnov (136) studied the polarization of thoriated oxide carbon anodes in molten chloride at low current density. Pletenev & Rozov (137) considered cathodic polarization during electrolysis of fused salts and concluded that prior data contained a small error caused by a potential drop of ohmic nature. Esin & Toporishchev (138) measured concentration polarization at high temperatures in fused oxides, generally complex silicates. Suski (139) studied the mechanism of the cathodic process on an iron electrode in the

electrolysis of a fused mixture of sodium and calcium chlorides. Stein (140) recently discussed the mechanism of various electrode reactions and described the discharge of lead in a fused NaCl-KCl solution.

In a beautiful piece of work, Flengas & Rideal (126) carried out potentiometric titrations of silver halides and cyanide in fused $NaNO_3$-KNO_3 mixtures. Sharp endpoints were obtained at stoichiometric equivalence; the titration curves were quite analogous to aqueous titrations. They obtained solubility products and reported that the relative order of solubility of AgCl, AgBr, and AgI is the same as in aqueous solution. Values for heats of solution were obtained from temperature coefficients of solubility. Flengas & Rideal found a very clear indication for the existence of the complex ion $Ag(CN)_2^-$. In titrating Ag^+ with CN^-, they obtained a sharp endpoint when one equivalent of CN^- had been added to one equivalent of Ag^+ and at this point there was a copious precipitate of AgCN. Further addition of CN^- resulted in a second endpoint at two equivalents of CN^-, at which point the precipitate of AgCN had redissolved forming $Ag(CN)_2^-$.

EQUILIBRIUM PROPERTIES

VAPOR PRESSURE

Vapor pressure studies up to December 1958 have been reviewed by R. F. Porter in the chapter on "Heterogeneous Equilibria and Phase Diagrams" in the *Annual Review of Physical Chemistry*, Vol. 10. Therefore, only the work of the past year on molten systems will be mentioned.

Cubicciotti & Keneshea (141), using a transpiration method, measured the vapor pressure of BiI_3 over Bi-BiI_3 solutions. Structural interpretations have been made based on vapor pressure data of the Bi-$BiCl_3$ system (142) and the Bi-$BiBr_3$ system (143) by Corbett (144), and later, in criticism, by Bredig (145), who proposes the presence of both the subhalide Bi_2X_2 and the dimeric metal Bi_2. The molecular beam studies of alkali halide vapors have continued by Kusch (146), and Eisenstadt, Rao & Rothery (147). Barton & Bloom (148) have determined the absolute vapor pressures for NaCl and KCl by a boiling point method and the apparent pressures from transpiration experiments. Assuming the presence of monomers and dimers only, the results give the vapor composition, equilibrium constants for dimer dissociation, and heats of dimer dissociation, the latter in reasonable agreement with molecular beam experiments.

THERMAL PROPERTIES

Thermal properties of molten salts such as heat capacities, heat content, heats of transition, and derived thermodynamic properties are periodically reviewed in the *Annual Review of Physical Chemistry* under the topic of "Thermochemistry and Thermodynamic Properties of Substances." In addition, phase diagram studies of solid-liquid equilibria and cryoscopy are reviewed under the topic of "Heterogeneous Equilibria and Phase Diagrams."

Janz, Solomons & Gardner (6) critically discussed cryoscopy of molten salts and reviewed the recent work in the field. This method of investigation is important because it provides information concerning the formation of complex ions, as shown by Van Artsdalen (12, 149).

ELECTROMOTIVE FORCE

Measurement of the electromotive force of a galvanic cell provides a direct method for obtaining the free energy change of the system and in turn the activities of ions in solution. In cases where the activity coefficient has deviated considerably from unity, the formation of complex ions has often been postulated. Daniell cells have also provided information on free energies of formation of molten salts. Thus, these measurements provide both information that is essential to developing the solution theory of molten salts and basic thermochemical data.

Bloom & Bockris (7) briefly discussed emf. measurements up to 1956. This review will cover the year 1957 to the present.

Laity (150) measured activity coefficients in the $AgNO_3$-$NaNO_3$ system in concentration cells with transference. Smirnov & Volchenkova (151) measured equilibrium potentials for oxide-carbon electrodes of Be in fused chlorides. Smirnov & Ivanovskii (152) measured the emf. of ThF_4 in KCl-LiCl eutectic. Mashovets & Revazyan (153) determined the emf. of cryolite-alumina solutions with various electrodes.

Flengas & Ingraham, using a Ag-AgCl reference electrode and an equimolar NaCl-KCl mixture as solvent, have studied the emf.'s of the systems: Co-CoCl$_2$ (154); Pb-PbCl$_2$, Zn-ZnCl$_2$, and Ni-NiCl$_2$ (155), Cd-CdCl$_2$ (156); Tl-TlCl, Cu-CuCl, Cu-CuCl$_2$, Cr-CrCl$_2$, and Cr-CrCl$_3$ (157); and Sn-SnCl$_2$, Fe-FeCl$_2$, and Mn-MnCl$_2$ (158). They also studied the redox potentials of the systems: Pt/CuCl, CuCl$_2$(KCl-NaCl) and Pt/CrCl$_2$, CrCl$_3$(KCl-NaCl) (157). Many of the above solutions are of interest because of the large deviations from ideality.

Markov (159) studied the emf. of the ZnCl$_2$-RbCl system to obtain thermodynamic properties of ZnCl$_2$. Senderoff & Mellors reported on a reversible chlorine electrode for emf. studies (160) and measured the emf. of Ce-CeCl$_3$ systems (161), finding evidence for unusual complex ions. Further evidence for complex ions in CeCl$_3$ was found in emf. measurements in CeCl$_3$-KCl and NaCl solutions (162). Markov, Delimarskii & Panchenko (163) studied several bivalent metal halides dissolved in alkali halides, again finding non-ideal behavior. Stern continued a series of emf. studies with a careful thermodynamic and kinetic study of the AgCl-NaCl system (164), and a study designed to evaluate liquid junction potentials (165). Hill, Porter & Gillespie (166) measured potentials for oxide formation of the metals Fe, Ni, Cu, and Au. Selis, Elliott & McGinnis (167) studied hygroscopic molten electrolytes to determine the behavior of hydroxide ions.

Sundheim & Rosenstreich (168) studied the thermoelectric potential of a simple molten salt thermocell and analyzed specific contributions to the

potential. Laitinen & Pankey (169) studied emf.'s of chlorine, bromine, iodine, iron, and vanadium systems in LiCl-KCl eutectic. Reference has previously been made to the table of emf.'s in LiCl-KCl eutectic by Laitinen & Liu (114). Wood (170) investigated a system with a Bi-Bi$_2$O$_3$-ZnCl$_2$ electrode as part of a study of ZnCl$_2$ as an electrolyte. Panish and co-workers studied the thermodynamic properties of AgCl-NaCl solutions (171) and of AgCl-LiCl solutions (172). Nikol'skaya, Lomov & Gerasimov (173) investigated thermodynamic properties of the Cu-Bi system dissolved in molten salts. Blander, Blankenship & Newton (174) studied solutions of AgNO$_3$ and KCl in molten KNO$_3$. The results of these experiments have been discussed in terms of a theoretical model derived by Blander (175). Several metal chlorides in LiCl-KCl eutectic have been measured by Yang & Hudson (176), who discuss results in terms of complex ion formation.

Gruen & Osteryoung (177) measured the emf. of the U-U(III) couple in LiCl-KCl eutectic. Piontelli (178) discussed general problems of reference electrodes in emf. studies. Bockris et al. (179) investigated electrode potentials of UCl$_3$, ZrCl$_4$, ThCl$_4$, and CeCl$_3$ in LiCl-KCl and NaCl-KCl eutectics. Flengas (180) measured electrode potentials of titanium chlorides in one to one molar KCl-NaCl solutions. Yang & Hudson (181) recently discussed the use of Ag/AgCl reference electrodes. Menzies et al. (182) measured the emf. for the redox equilibrium Ti$^{+2}\rightleftharpoons$Ti^{+3} in the LiCl/KCl eutectic vs. a Ag/AgCl reference electrode.

SOLUBILITY

A few papers have recently appeared on the solubility of metals in their molten salts. Corbett, von Winbush & Albers (183) studied the solution of the respective metals in molten PbI$_2$, SbCl$_3$, SbI$_3$, ZnCl$_2$, ZnI$_2$, CdI$_2$, and GaBr$_2$. The results are interepreted in terms of the formation of slightly stable subhalides. Evidence is also found for the formation of some gaseous subhalides. Johnson & Bredig (2) continued their investigations of miscibility of alkali metals with molten salts with a study of potassium-potassium halide systems. Mellors & Senderoff (184) studied the solubility of Ce in CeCl$_3$ and CeCl$_3$ in Ce without finding a consolute temperature which, if it exists, must be above 1000°C. Yosim et al. (185) made a phase equilibrium study of the Bi-BiCl$_3$ system, finding a consolute temperature of 780°. Druding & Corbett (186) measured the solubility of Nd in its halides. Such studies have bearing on other measurements in which the metal may be in contact with the salt, such as in emf. studies when dissolution of the metal electrode changes the properties of the melt, or in all cases where a metal container is used for the molten salt.

Duke & Iverson (187) measured the increase in solubility of bivalent metal chromates in KNO$_3$-NaNO$_3$ eutectic as halide ion was added. The results were interpreted in terms of complex ion formation, but since no correction was made for non-ideality of the solution, the interpretation cannot be regarded as conclusive.

Miscellaneous studies of solubility involve the measurements of solubility of water in molten mixtures of LiCl and KCl (188) in alkali nitrate mixtures, and in lithium perchlorate (189), and of noble gases in molten fluorides (190, 191). Flengas (192) measured the solubility of $TiCl_4$ in KCl-NaCl mixtures.

DENSITY

Aside from describing a fundamental property of material, density measurements are important for determining derived quantities such as equivalent conductance. It is of interest to compare transport quantities on the basis of equal molar volumes. Density values of molten alkali halides have been determined accurately for pure salts (40, 43) and some binary mixtures (43) by Van Artsdalen and Yaffe. The densities of a few other pure salts have been accurately measured [see Bloom & Bockris (7)], but mostly these determinations are in error. Husband (193) measured densities for $NaNO_2$, KSCN, and $KClO_4$ and described the apparatus used. Keneshea & Cubicciotti measured densities of Bi-$BiCl_3$ (194) and Bi-$BiBr_3$ (195) mixtures and observed deviations from additivity and unusual partial molar volume behavior. Senderoff & Mellors (196) also observed unusual density behavior in the Ce-$CeCl_3$ mixture.

Schinke & Sauerwald (197) have made a definitive study of volume changes on melting for a large number of salts which are in fair agreement with the values determined by Landon & Ubbelohde (198).

SURFACE TENSION

Several early workers measured surface tension of many fused salts. A favorite technique was to use the maximum bubble pressure method since this does not require visual observation of the hot liquid. It is strongly suggested from other studies using tracer techniques that materials are frequently strongly adsorbed in the surface layer of fused salts. Thus, trace impurities may be expected to exert profound influence of the surface tension of a melt. Most of the early studies of fused salts were made without benefit of ultra-purification procedures now generally accepted as necessary for definitive investigations. Consequently, we must view early measured values of surface tension as approximate.

The problem of the surface tension of pure fused salts and of mixtures of fused salts has not received adequate theoretical treatment and, as a result, interpretations based on observed deviations from additivity in mixtures must be regarded as speculative. Boardman, Palmer & Heymann (199) measured the surface tension of a number of mixtures of molten salts and compared the results with a theoretical equation of Guggenheim (200) for an ideal binary mixture. Strong deviations were ascribed to complex ion formation, except in the case of silver salt mixtures, for which large negative deviations were observed. Thus, the situation arises in which similar surface

tension behavior for different systems may be due to different physical phenomena.

Desyatnikov (201) measured surface tension for the ternary system KCl-NaCl-MgCl₂ and observed deviations from additivity. Ellis, Smith & Baker (202) measured surface tensions of a series of pure alkaline earth metal halides as a function of temperature. Dahl & Duke (203) measured surface tensions of AgNO₃ mixed with NaNO₃ and KNO₃ and observed small deviations from additivity. The same authors (204) measured mixtures of PbCl₂ with alkali metal chlorides and observed increasing deviations from additivity as the size of the alkali cation was increased. Peake & Bothwell (205) studied the KCl-BaCl₂ system and observed non-linear variations with increasing mole fraction of solute.

SPECTROSCOPY AND X-RAY DIFFRACTION

Visible and ultraviolet spectroscopy.—Spectroscopy of solid salts has received much experimental and theoretical attention. In general, little or no absorption of visible light is observed, but a series of intense absorption bands occurs in the ultraviolet region and is followed by a region of continuous absorption extending to shorter wavelengths. This series of bands has been ascribed to exciton levels lying below the conduction band. A tail on the long wavelength side, the position of which is temperature dependent, is also observed. This dependence is ascribed to the increasing numbers of lattice defects with temperature, which act as electron traps lying above the valence band in energy; thus, transitions to exciton levels below the conduction band are correlated with absorption of longer wavelength light. One does not observe discrete bands from this source because of the various natures and environments of the traps. Another feature of the bands is a broadening as the temperature is increased. This is due to thermal alteration of the exciton levels.

Mollwo (206) in 1948 prepared a spectroscopic cell to observe the changes in the ultraviolet spectrum of KBr, KCl, and KI as temperature increased through the melting point. The cell was one millimeter in length, too long a path to observe the exciton band structure. Therefore, the only measurable quantity was the position of the band edge, which was observed to shift continuously toward the red as the temperature was increased up to the melting point. However, as the solid melted, a discontinuous red shift of the band edge of about 0.7 ev was observed. As noted by Mollwo, this was much too large a change to imply any simple correlation with the melting process since the heat of fusion of these materials is only of the order of 0.2 ev. Later studies of the dependence of the absorption edge on temperature were made by Sakai (207 to 210) whose study included nitrates, chlorides, bromides, and iodides of alkali and alkaline earth metals. Discontinuities at the melting points were not observed, although plots of the frequency of the band edge vs. temperature became non-linear for most molten salts.

Sundheim & Greenberg (211) studied the behavior of the band edge with temperature for several salts and also found the red shift. They also attempted to look for structure in the region of the high energy side of the absorption edge, seeking analogies with the exciton bands of the solid. They were unable to construct a cell thin enough to observe anything but complete absorption, although they believed that the temperature dependence of the band edge was due to a broadening of exciton levels. They also observed a dependence of the band edge on concentration for a solution of AgCl in lithium-potassium chloride eutectic. In a later study of solutions (212) these authors used a double beam instrument, placing the pure solvent in the reference compartment and the solution in the sample compartment. In all cases, they observed an absorption peak whose maximum appeared to lie just to the low energy side of the band edge of the pure solvent. It would seem that the opaqueness of both solution and solvent to the high energy side of the band edge could account for the decreasing portion of the peak on the high energy side, and thus the aspect of the spectrum modified by instrumental effects. In this case, the observed peak could not be unequivocally described as an exciton or charge transfer band. Thus, before interpretation is possible, the ultraviolet absorption region for molten salts will require further study, with samples thin enough that the intense absorption region may be measured. Sakai (213 to 215) has also studied solutions of molten salts and made comparisons of the band edge position with concentration as an indication of structural changes.

Somewhat more revealing studies of solutions of transition metal ions in molten salts have been made by Gruen (216 to 218), Boston & Smith (219), and Sundheim & Harrington (220); and of actinide and rare earth ions by Gruen (221, 222). It is suspected these ions form complexes in analogy with their behavior in aqueous solution. Ni (II) ions in the presence of Cl⁻ seem to have received the most attention (216 to 220) and the most recent work (220) has shown fair agreement of the spectrum with a ligand-field theory calculation of energy levels for tetrahedrally coordinated $(NiCl_4)^{2-}$ complexes. A more complete investigation of the near infrared region might help to fix this assignment of the structure. Sundheim (223) has recently gathered the spectra of transition ions in molten salts and discussed assignments based on ligand-field theory.

Other studies in the visible region have been of sulfur in eutectic solution (224) and of halogen gases in eutectic solutions [Greenberg & Sundheim (212)]. Smith & Boston (225) measured the spectra of nitrate, nitrite, and chromate ions in fused salt mixtures and found a close relationship to the spectra in aqueous solutions.

Raman spectroscopy.—The studies of vibrations of polyatomic species in molten salts have made use of the Raman effect, but not of infrared techniques, because of difficulties in finding suitable materials for optical windows or an optical arrangement to circumvent the difficulty. Woodward and co-workers have studied the Raman spectra of molten $GaCl_2$ (226) and $GaBr_2$

(227) and have found an excellent correspondence with the spectra of $(GaX_4)^-$ ions and $(GaBr_4)^-$ ions in aqueous solutions.

Bues (228) has studied mixtures of $ZnCl_2$-KCl and $CdCl_2$-KCl. Unfortunately, the experimental data are meager with only one or two bands appearing for various compositions. On the basis of the shifts of one of these bands, Bues has concluded that the structures, associated $ZnCl_2$, $(ZnCl_3)^-$, and $(ZnCl_4)^-$, exist for $ZnCl_2$-KCl and associated $CdCl_2$, $(CdCl_3)^-$ for $CdCl_2$-KCl. Bredig & Van Artsdalen (229) have examined the data and believe that $(CdCl_3)^-$ and $(ZnCl_3)^-$ are unlikely to be present and that the tetra-coordinated complexes are more likely to exist. Bues (230) also observed the Raman spectra of the nitrate ion in $LiNO_3$, $NaNO_3$, KNO_3, and $AgNO_3$ melts as well as in $AgNO_3$-KNO_3 solutions and aqueous solutions as a function of concentration. An interesting correlation of the symmetric stretching vibration frequency with the free volume of the melt was observed, and other spectral details discussed qualitatively led to the conclusion that all these melts were completely dissociated into cations and nitrate ions.

A series of papers by Gerding & Houtgraf (231 to 233) has dealt with compounds not generally thought of as salts, but based on Raman spectra show strong evidence of having an ionic nature. Thus, in the systems $NaCl \cdot AlCl_3$ and $NOCl \cdot AlCl_3$ one is led to the structures $Na^+(AlCl_4)^-$ and $NO^+(AlCl_4)^-$. $TeCl_4$ and $SeCl_4$ are given the structures $(TeCl_3)^+Cl^-$ in the liquid and solid and $(SeCl_3)^+Cl^-$ in the solid state. Also, the systems $TeCl_4 \cdot AlCl_3$ and $SeCl_4 \cdot AlCl_3$ have the structures $(TeCl_3)^+(AlCl_4)^-$ and $(SeCl_3)^+(AlCl_4)^-$ in the liquid and solid.

Other spectroscopic methods.—Rowland & Bromberg (234) have described the application of nuclear magnetic resonance to the study of molten salt systems. The resonance spectrum of ^{205}Tl was observed in the salts TlCl, TlBr, $TlNO_3$, Tl_2Cl_4 and Tl_2Br_4. The compounds Tl_2X_4 are mixed salts of TlX and TlX_3. Only two lines are observed, indicating the presence of only two thallium species. A chemical shift, proportional to the electronegativity of the halide, is observed in the simple salts between the liquid and solid at the melting point. This proportionality is interpreted as being attributable to a removal of effective covalent bonding in the liquid compared with the solid.

Bloom & Rhodes (235) have discussed the measurement of refractive index and find molar refractivities to be nearly additive for nitrate mixtures.

X-ray diffraction.—In recent years several x-ray diffraction studies have been made of molten salts. Zarzycki (236 to 239) has studied alkali halides and alkaline earth halides, as well as vitreous SiO_2 and GeO_2. Wood & Ritter (240 to 242) have studied CdI_2, InI_3, and SnI_4. Danilov & Krasnitski have studied alkali nitrates (243). Levy *et al.* (244) made comprehensive studies of alkali halides by both neutron and x-ray diffraction. By the use of diffraction methods and certain assumptions, one can estimate the average interionic distances and the average number of neighbors. The poor resolution that is characteristic of liquid diffraction studies makes this procedure some-

what arbitrary. For example, even though the experimental data of two experimenters may agree, their interpretation of the average number of neighbors may not. Thus, it would appear that the greatest quantitative usefulness of this technique would lie in testing theories of the radial distribution function for liquids. One very general result from Levy's work (244) is that the average coordination number in the liquid is reduced below that in the corresponding solid, e.g., from six to a little over four in several cases. The second general result is that the average internuclear distance in a salt also decreases in going from solid to liquid, despite the fact that the molar volume increases. This must be interpreted as favoring the existence of many holes in the liquid, viewed otherwise as a rather disordered, short-ranged, quasi-lattice structure.

THEORY OF FUSED SALTS

An equilibrium theory of pure molten salts should be capable of predicting thermodynamic properties and should provide a relation between state properties, i.e., pressure, temperature and volume. The method for deriving such a theory can proceed along several different lines in analogy with progress in the theory of normal liquids. The most general approach would be to extend the radial distribution function theory to the case of dissociated molten salts. Such an extension would be difficult, but work in this direction was proceeding in the laboratory of Professor J. G. Kirkwood (personal communication) before his untimely death. It is hoped that this approach can be brought to fruition as it could lead to an insight into the structure of melts, as well as provide a rigorous basis for interpretations of observed radial distribution functions from x-ray and neutron diffraction experiments. A second, less general approach would be to take a specified model of the molten salt and attempt to derive a partition function from molecular motions appropriate to the model. Thus, the cell model or the hole model, in principle, could be generalized for molten salts by assuming a lattice of cells similar to that found in the solid. The potential energy expression of the particle within the cell would be complicated by the presence of long range coulomb forces and the sort of averaging procedure used for normal liquids in the cell model and the hole model probably would not be suitable. Another liquid state model that is similar in many ways to the approximation of Ono (245) for the hole model is the theory of significant structures of Eyring, Ree & Hirai (246). This theory relies somewhat more on empiricism than the above theories, but has shown good agreement with experiment. Recently Blomgren (247) extended this theory to the case of molten salts and showed its applicability to transport phenomena for normal liquids. The results for molten salts were incomplete, but did show promise of correlating state properties as well as predicting thermodynamic properties. Carlson, Eyring & Ree (248) very recently extended this same theory, but in a different manner from Blomgren. These authors included a rather large contribution from alkali halide molecules in the partition function for the liquid and used a

different potential energy expression, thereby adding another parameter. The existence or nonexistence of molecules in the liquid is difficult to establish theoretically, although experimental evidence points to a basically ionic nature for the liquid. A largely empirical treatment based on measurements of ultrasonic waves in molten salts was given by Bockris & Richards (249). An approximate expression related the free volume, assumed to be identical for cation and anion, to the velocity of sound in the molten salt. This free volume was then used in the early cell theory partition function of Eyring & Hirschfelder (250). Rough estimates of entropy and heat capacity were made by this method. An equation of state by Buehler *et al.* (251), was also tested and a fairly constant value of the molar gas constant was found, indicating the range of validity of the equation of state.

Also of theoretical interest is the problem of the melting of ionic crystals. Ubbelohde (252) has recently reviewed the current thought on the problem and concluded that the theory of fusion of salts should now be sufficiently advanced to begin to compute quantitatively specific contributions to the heat and entropy of fusion. This does not include the prediction of the phase transition itself by statistical mechanics; the great difficulties of that problem in normal liquids would be compounded in molten salts.

As is the case for normal liquids, the theory of mixtures of molten salts has progressed somewhat more rapidly than that of the pure liquid. Temkin (253) treated the case of ideal mixtures and proposed a lattice model as the solution. The model, which has served as the basis for all later theories, invokes two interpenetrating lattices, an anion lattice and a cation lattice. Mixing of anions can occur only on the anion lattice and of cations only on the cation lattice in such a way that no cations ever occur on the anion lattice or *vice versa*. This situation becomes complicated even in the ideal case when a mixture of univalent and bivalent anions, or cations or both is considered. Forland (254) treated this problem for ideal solutions by considering the mixing of a vacancy for each bivalent ion if the basic lattice is determined by univalent ions. Two possibilities arise, the bivalent ion can occupy two adjacent lattice positions, in which case the vacancy always remains adjacent to the bivalent ion, or the uni- and bivalent ions can mix randomly. The latter case seemed to be supported better by thermodynamic data. Flood & Urnes (255) also found support for this model. Flood, Forland & Grjotheim (256) considered the case of random mixing, resulting in an ideal entropy of solution and nonzero heat of solution. This is commonly called the zeroth approximation in the theory of strictly regular solutions. The result comes out in very simple form and is probably an adequate description of slightly nonideal solutions. Blander (175) has criticized this formulation and has shown the lack of agreement of this treatment with activity coefficient data taken on the $AgNO_3$-KNO_3-KCl system (174); however, the agreement would have been better had he chosen a different value for the interaction energy. Blander then proceeded to develop a solution theory somewhere in between the zeroth approximation and the quasi-chemical or first approximation.

The theory only applies to dilute solutions and the range of validity is not clear. In a more recent paper, Blander & Braunstein (257) developed a solution theory based on the quasi-chemical approximation. They compared the results for the activity coefficient of $AgNO_3$ in the systems $AgNO_3$-KNO_3-KCl and $AgNO_3$-$NaNO_3$-NaCl with the two theories and found that the earlier theory agrees better with the K^+ system and the later theory with the Na^+ system. Further experimental work to distinguish between the applicability of these theories would be interesting.

Further work on solutions by Flengas & Rideal (126), indicated that the Born theory of solvation should be applicable to molten salts; and Rastogi & Varma (258), have calculated lattice energies for molten mixtures of electrolytes.

The development of solution theory has an important bearing on the problem of complex ion formation. Measurements of emf. that show deviations of activity coefficients from unity have often been cited as evidence for complex ion formation. As discussed above, however, nonideal behavior can occur in systems in which the presence of complex ions is very unlikely. Therefore, it is important to find better criteria for establishing the existence of complex ions. A recent discussion of this problem by Van Artsdalen (11) considered evidence that has been considered valid for the indication of complex ion formation. Another review of the structure of molten salts by Watelle-Marion (8) discussed the central problems of structure determination, identification of structural elements, nature of inter- and intramolecular forces, and distributions of particles; and described experiments designed to elucidate these problems. It is clear, however, that proof of complex ion formation in molten salts has been elusive, and probably awaits further development of spectroscopic techniques.

SUMMARY

Let us summarize briefly some of the more significant advances of recent years in the study of fused salts. Precise methods employing improved techniques have become available for many different physical-chemical measurements. Precise automatic control of temperature has become routine. The preparation of high purity materials has been achieved. New techniques have included vacuum studies, the use of inert atmospheres and particularly electrolytic purification procedures. Recent very precise cryoscopic studies have contributed to our understanding of melts. The development of techniques for measuring self-diffusion in molten salts makes it possible to obtain valuable new information on transport properties. The development of x-ray techniques to elucidate structure of molten salts has been a significant achievement and the applications of various types of spectroscopy are beginning to yield important data, particularly with regard to the structure of complex ions. Improved analytical techniques have been developed. Finally, foundations are being laid for sound statistical and theoretical treatment of molten salts. These include development of equations of state,

and the determination of structure, transport, and thermodynamic properties.

Unquestionably we are on the verge of important developments and discoveries relating to fused salts. Indeed, the reliable measurement of almost any property of a fused salt is important, since detailed data are lacking on so many properties and for so many systems. We suggest that the next few years will bring a much better understanding of structure as a result of many different types of study, including especially x-ray diffraction and spectroscopy. We believe that investigation of all types of transport processes in fused salts will be very important and will lead to further development of relationships among the various transport phenomena. Perhaps the largest area of general interest to chemists and to industry will be studies of chemical reactions, including their kinetics, mechanisms, and thermodynamics. It seems quite likely that as our understanding of the electrochemistry of molten salts becomes clearer, we will also gain more insight into the structure and electrochemical behavior of concentrated aqueous solutions of electrolytes.

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KINETICS OF REACTIONS IN SOLUTION[1]

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Following the tradition of treating at least one field with relative thoroughness, we shall concentrate mainly on studies of fast reactions in solution and some basic mechanisms in aqueous systems such as substitution in ion complexes, redox, and protolytic reactions. The time period covered will exceed that of last year somewhat, as the work in this field has not recently been treated as a whole. The survey of literature includes some papers of 1960 that were already available.

If the interest of the scientific public in certain fields is reflected by the number of conferences and symposia, 1960 seems to be especially suitable for a review of these subjects. Besides the large congresses of the different national and international chemical organizations, the International Congress on Coordination Chemistry (London, Spring 1959) and the Seventeenth Conference of the International Union of Pure and Applied Chemistry (Munich, Fall (1959) deserve special mention; several special colloquia and symposia in the above mentioned fields were held. The Faraday Society conducted a general discussion with the title: "Energy-Transfer with Special Reference to Biological Systems" in the Spring of 1959, in which more than 12 papers dealt with the kinetics of fast reactions in solution. The Bunsen-Gesellschaft and the Max-Planck-Gesellschaft sponsored an International Colloquium on "Fast Reactions in Solution" (Fall 1959) with more than 30 papers in the field. The papers of both meetings have been published in special issues of the *Discussions of the Faraday Society* (1) and the *Zeitschrift für Elektrochemie* (2), respectively, which have the character of monographs covering the whole field. Among symposia on the second part of our subject (basic mechanisms in aqueous systems) two special meetings should be mentioned. The publications of these became available during the last year: "Symposium on Mechanisms of Inorganic Reactions in Solution" (American Chemical Society, Summer 1958) (3) and "Symposium on Charge Transfer Processes" (Canadian Institute of Chemistry, Fall 1958) (4).

FAST REACTIONS

Publications in this field of chemical kinetics have increased primarily as a consequence of the improved instrumentation that led to higher time

[1] The survey of literature pertaining to this review was concluded with the October 1959 issues of Chemical Abstracts, so far as general aspects are concerned.

[2] Operated by the Union Carbide Corporation for the U. S. Atomic Energy Commission.

resolution and sensitivity. Therefore, it seems appropriate to classify the papers in this survey according to the methods used. The applications, which are discussed in this connection, will deal with kinetics of inorganic as well as of organic or biochemical reactions.

The two problems in studying fast reactions are: (*a*) to initiate the reaction, e.g., by mixing the components; and (*b*) to follow the course of the reaction by some charactristic parameter of the mixture. Since physical properties such as conductivity, emf., light absorption, and optical rotation can be recorded very rapidly by modern electronic devices, (*b*) usually is not the time-limiting problem. It is more difficult to initiate the reaction "instantaneously" (i.e., much faster than the reaction proceeds).

Mixing techniques.—Hartridge and Roughton first tried to solve the problem for reactions in the liquid state more than 35 years ago; they used the flow technique, which is well known to chemists today. Roughton, in a short historical review (5), outlined the biochemical problems that led to the development of the technique and its present state of application.

The greatest time resolution of this method still lies in the region of the millisecond, the major limitations being incomplete mixing and cavitation at high flow rates. Most of the recent technical refinements are concerned with an increase of sensitivity in recording and with combining the method with new techniques for following the reaction. Brilliant spectrophotometric techniques (double beam, visible and ultraviolet region) for following fast absorbency changes have been developed by Chance and co-workers and are described in a comprehensive article (6). The oscillographic recording of complete (visible and ultraviolet) absorption spectra of short-lived intermediates in the flow tube is described by v. Bünau, De Maeyer & Matthies (7). Optical absorption and conductivity measurements in combination with a stopped flow technique [as described also by Sirs (8)] are used by Prince (9, 10, 11) in the study of substitution reactions of organometallic halides [cf. Johnson & Schmall (12)]. Very considerable improvements in the detection of small amounts of intermediates have been made by application of microspectrometric methods, as described by Chance *et al.* (13) and by Chance & Legallais (14). Such methods are capable of detecting as little as 10^{-20} moles of a substance (e.g., cytochrome or reduced pyridine nucleotide) having half lives of only a few seconds. This opens new possibilities of extending the measurable range of chemical kinetics. Chance (6) and Brill (15) describe a method for rapid measurement of small changes of volume magnetic susceptibility in a flow system using the Rankine balance technique. The time resolution is between 40 and 100 msec. Application has been made to reactions of cuprous laccase with oxygen forming cupric laccase and to the cytochrome oxidase system.

If short-lived intermediates of radical nature occur in a reaction, the combination of flow methods with electron spin resonance techniques is of advantage. Studies of this type have been described by Venkataraman & Fraenkel (16) [cf. Blois (17), Wertz (18)]. These authors detected the benzo-

semiquinone as a short-life intermediate in the oxidation of benzo-hydro-quinone to benzo-quinone. Similar studies with ascorbic acid and dihydroxy-fumaric acid are reported by Yamazaki & Mason (19) and are also being carried out in Chance's laboratory.

Biochemists often are interested in following changes in absorption spectra in complete cell systems (e.g., if reacting substances diffuse into the cells). The requirement of measuring a series of complete absorption spectra within .1 to .01 second is fulfilled by an ingenious method developed by Niesel, Lübbers & Thews (20). The fast scanning of the spectrum is effected by a vibrating mirror (100 c./sec.) deflecting the light beam across the slit of the monochromator. A second mirror vibrating at 20 kc./sec. alternates the light between the absorption cell and a reference cell. The logarithm of the quotient of both intensities is directly recorded on an oscilloscope. Studies with intact red blood cells are reported.

Most applications of flow methods deal with fast biochemical processes for which this technique was originally developed. Even these original problems continue to be of interest to experimenters as Roughton has shown (5). The problems now being studied are much more subtle. Gibson, Rossi-Fanelli & Antonini (21) describe some recent studies on the reactions of haemoglobin in red blood corpuscles. Many interesting applications are to be found in the field of enzyme kinetics. The work of Chance and his school (*loc. cit.*) has demonstrated the great versatility of the technique when applied to this field. Applications to inorganic reactions [cf. Wahl (229)] are discussed below.

The flow technique, which utilizes the classical principle of initiating a reaction by mixing the partners, extended the measurable range of kinetics down to about 1 msec. Any further extension to shorter times requires some new principle avoiding the mixing problem. Two basically different approaches have proved useful and must be discussed:

(*a*) Information about the reaction can be obtained from competition with a physical process of which the time constant is known. We shall call methods utilizing this principle "competition methods."

(*b*) The chemical rate process can be directly recorded as an equilibration process following fast perturbation of an equilibrium or stationary state (e.g., by changing external parameters which determine the state, or by irradiation). We may call this group "perturbation methods"; they represent direct methods, regardless of whether we follow the process with time or with the reciprocal of time, i.e., the frequency.

Competition methods.—Let us begin with a review of studies in the first group. Competition with transport processes such as diffusion or ionic migration is the base of the different Electrochemical Methods. Recent comprehensive reviews on the different techniques are available [Brdička (22), Koryta (23), Gerischer (24), Gierst (25)]. Brdička and Koryta describe the use of polarographic currents, which are influenced by chemical reactions involved in the depolarization process, for determining rate constants of

rapid reactions. A more extended theoretical treatment is given by Čižek, Koryta & Koutecký (26). The very elegant methods, mainly developed by the Czechoslovakian school, has become very useful for the study of quite a number of chemical reactions, including metal complex formation [as studied especially by Koryta (27, 28)]; redox reactions [Brdička (22), Matyska (29), Brežina (30)]; acid-base transformations [cf. Nürnberg, van Riesenbeck & v. Stackelberg (31)] including tautomeric transformations [studies of 2-keto-L-gulonic acid by Los & Gaspar (32, 33)]; and hydration [studied with α-oxocarbonic acids by Becker & Strehlow (34)]. Results obtained by the so-called method of catalytic currents [cf. (22)] yielding second-order rate constants of 10 to 10^4 M^{-1} sec.$^{-1}$ are usually very reliable. However, in the fastest processes such as protolytic reactions the conditions necessary for a study of the homogeneous reactions are not always fulfilled so that the corresponding data are not very precise. A formal interpretation of the results then may lead to meaningless results. [For example, Tanaka & Murayama (35) report a rate constant of HCN-dissociation of 1.00 (!!!) $\times 10^7$ sec.$^{-1}$ (at 25°C.). With an equilibrium constant of 7.2×10^{-10} M the recombination rate constant would have a value of 1.4×10^{16} M^{-1} sec.$^{-1}$, which is higher by at least five orders of magnitude than the theoretically highest possible value for a diffusion controlled reaction.] The limitations of the method are carefully analyzed by Strehlow (36). Improvement in the evaluation in certain cases can be obtained by considering the buffer reactions in more detail [Becker & Strehlow (37)]. In so far as relevant kinetic data from direct methods are available, the more complicated situation of such a multiple-step reaction system may be analyzed.

Besides the polarographic methods, the galvanostatic and potentiostatic techniques deserve mention. The influence of a homogeneous chemical reaction on the temporal course of an electrode reaction at constant potential is discussed by Gerischer (24). Results for the rate of complex formation between $Cd(CN)_3^-$ and CN^- are reported. Gierst & Hurwitz (25) give a more extensive theoretical treatment of double layer corrections in the evaluation of rate data and discuss some potentialities of the galvanostatic method. Delahay & Oka (38), using the potentiostatic method, obtained some results for the dissociation of monochloracetic acid in a 50-50 water-ethanol mixture. The value of the recombination rate constant (1.3×10^{10} M^{-1} sec.$^{-1}$) is of the expected order of magnitude, though it seems a little low compared to the known value for acetic acid. Further results for acetic and formic acid obtained by the galvanostatic method are discussed by Giner & Vielstich (39). The rate constants for acetic acid agree well, but those for formic acid less well, with the values obtained by direct methods (102). Current-voltage measurements with a rotating electrode [for theory cf. Levich (40), Koutecký (41), Dogonadze (42)] are applied to the same systems by Vielstich & Jahn (43) and yield results that are in good agreement with those of direct methods. Current-time measurements at the dropping mercury electrode are

also used by Berg & Kapulla (44) to analyze simultaneously occurring homogeneous reactions.

In the methods mentioned above, the competition process takes place in the close vicinity of the electrode, i.e., the "reaction layer." The applicability of these methods depends largely upon the exactness of the theory by which these parameters are calculated. Difficulties of this kind are avoided in a high-field method based on a similar principle, i.e., using the competition between ion migration (at high electrical field strength) and chemical reaction (charge production by dissociation). But here the competition occurs in the (well defined) space between the electrodes, and the rate of dissociation is measured as a saturation current. In aqueous systems it is not possible to reach high enough electrical fields, so, unfortunately, the method cannot be applied to these systems. It has been used successfully, however, to study dissociation and proton transfer in ice crystals [Eigen & De Maeyer (45)] and is being employed to study dissociation processes in nonaqueous solvents [cf. De Maeyer & Bayles (46)].

Dubois (47) and Walisch (48) used a method which in principle may be considered as an inverse to the above: Instead of measuring the production of a substance by a stationary current, the rate of consumption of a reactant is balanced by its electrolytic production in the cell. More specifically, Dubois studied the bromination of olefines and NN-dialkylanilines in aqueous solution. Instead of recording the time dependence of the bromine concentration by potentiometric recording, he kept it at a constant value by means of an electrolysis process. This coulometric recording yields results in satisfactory agreement with previous studies of Bell & Ramsden (49) who used potentiometric recording. The rate constants obtained by these methods are quite high (10^6 to 10^9 M^{-1} sec.$^{-1}$) though the actual half times are not very short. The trick consists of using a very small concentration of reactants and a sensitive method of detection. Bell's investigations show that where these conditions apply, even classical techniques allow the determination of large rate constants.

The principle of keeping the concentration of a reacting species constant has also been used by Kahlweit (50) in nucleation studies where the critical ion concentration is maintained by applying an electric field to ion exchange membranes, the electric current being the measurable parameter.

Instead of matter transport, energy input may also be utilized to maintain a stationary state of a reacting system. In photochemical systems a steady influx of light quanta will produce a photostationary state, the determination of which (in combination with quantum-yield measurements, e.g., by scavenger methods) allows rate studies. Among contributions in this field we should like to focus attention upon the very systematic studies of Noyes and his co-workers (51, 52). By measuring quantum yields for dissociation, Noyes (53) tested solution models and found that for the fast recombination of fragments proximity effects may modify the usual picture

based on an equilibrium spatial distribution. Also Schenck and co-workers [for review on previous literature cf. Schenck & Koch (54)] used stationary measurements in order to obtain information about fast processes, especially of cyclic intermediate catalysis by sensitizers in the photochemical combination of organic acceptors with O_2 to peroxides.

A competition between the known lifetime of an electronically excited state and a reaction of the excited molecule, resulting in changes in the fluorescence spectrum, can be used for determining reaction times of the order of 10^{-8} to 10^{-9} sec. Weller (55, 56, 57) measured rate constants of protolytic reactions of excited molecules by studying such fluorescence transformations. In cases where fluorescence can be measured, the method yields very precise results, some of which are discussed below [cf. Weller (58)].

Viscosity and temperature effects in fluorescence were studied by Bowen (59). Problems of energy transfer for excited molecules are excellently reviewed in two articles by Förster (60, 61). These fast electronic excitation transfer processes may be of general importance for biology [Szent-Györgyi (62)]; their occurrence in photosynthesis (cf. below) is well known.

A more detailed treatment of this fascinating field would be beyond the scope of this article so we can only refer to relevant literature that is quoted quite extensively in (1). A few more papers concerned with fast homogeneous photochemical reactions will be considered in connection with a review on flash photolysis studies.

Other examples belonging to the group of competition method are provided by nuclear magnetic and electron spin resonance techniques. Separated resonance lines of two chemical states, between which transformations are possible, can only be observed if the transformation frequency is slow with respect to the frequency separation of the two lines. Fast transformations will cause line broadening and a disappearance of the discrete structure of the spectrum because of competition between the resonance process and chemical transformation time. Among recent theoretical contributions to the problem of line broadening are the papers of McConnell (63), Sack (64), Kaplan (65), Piette & Anderson (66). Eyring *et al.* (67) discuss problems of line broadening and molecular kinetics in the light of absolute rate theory.

Weissman (68) described several cases of the use of electron spin resonance. The occurrence of electron transfer processes in the time range between 10^{-4} and 10^{-9} sec. produces observable effects in the resonance spectra. Detailed information concerning the mechanisms, not amenable to standard kinetic methods, could be obtained. Some of the applications [cf. Ward & Weissman (69)] are discussed in the section on redox reactions.

Applications of nuclear magnetic resonance technique to rate studies have been even more popular. The theoretical calculations mentioned above follow the basic investigations on proton magnetic resonance of Gutowsky and his school, which have been discussed in earlier reviews [for earlier literature cf. Gutowsky & Holm (70)]. Very straightforward applications to proton exchange processes have been described recently by Meiboom (71) and co-workers, including the systems ammonia [Meiboom, Loewenstein &

Alexander (72)], the methyl-substituted amines [Grunwald, Loewenstein & Meiboom (73), Loewenstein & Meiboom (74)], and N-methylacetamide [Berger, Loewenstein & Meiboom (75)], all in aqueous solution. Other papers deal with proton exchange rate studies in the systems water-hydrogen peroxide [Anbar, Loewenstein & Meiboom (76)] and methanol-water [Luz, Gill & Meiboom (77, 78)]. These studies add valuable new information to our knowledge about protolytic reactions (cf. below). Processes of this kind, i.e., the proton exchange between identical particles, usually cannot be studied with the other methods mentioned in this article. The NMR-results fit well into the picture obtained by studies of proton exchange between unlike particles, though sometimes the definition of the process we usually call the "protolytic reaction" differs somewhat from that studied by spin resonance methods [cf. Eigen (79)].

Further interesting NMR-work is to be mentioned: Patterson & Ettinger (80), using C^{13} isotopes, studied the water-carbon dioxide equilibrium. Their results on the relative concentrations of the different entities are consistent with predictions from other data. Studies with carbonic anhydrase may yield new information that is not obtainable by other techniques. The paper of Patterson & Ettinger includes a detailed theoretical analysis of the method of evaluation.

The influence of paramagnetic ions in solution on the line shape of a nuclear magnetic resonance signal, which depends either on the rate of transverse relaxation of magnetization of nuclei close to the ion or on the rate of exchange of such nuclei with more distant ones, can be used to estimate exchange rates from coordination spheres. Such applications are discussed by Broersma (81), Connick & Poulson (82), Bernheim et al. (83), and in a comprehensive paper by Pearson et al. (84) [reporting also data of Morgan & Nolle (85)]. This method seems to be very promising for providing new information that cannot be obtained by standard techniques. However, a few inconsistencies at the present time still seem to require some explanation (cf. the section on substitution reactions). An ingenious method for measuring resonances of water molecules bound in coordination spheres of metal ions has been reported by Jackson, Lemons & Taube (86). By adding the paramagnetic Co^{3+}-ion in high concentration to the O^{17}-enriched water, the (O^{17}-) solvent water resonances can be shifted sufficiently so that the peaks due to water molecules bound in the coordination spheres of cations become distinguishable. The method allows discrimination of two groups of metal ions; the first group (Mg^{+2}, Sn^{+2}, Ba^{+2}, Hg^{+2}, Bi^{+3}) exchanging its coordinated water molecules faster, the second (Be^{+2}, Al^{+3}, Ga^{+3}) exchanging them slower, than 10^{-4} sec.

Exchange-rate measurements that utilize the line broadening due to shortening of the phase memory caused by quadrupole coupling with nuclei were reported by Hertz (87). According to his data, the formation of the various Cd-bromide complexes is a very rapid process having rate constants of the order of 10^8 to 10^9 M^{-1} sec.$^{-1}$. Myers (88) previously used this method to determine the rate of the reaction $I_2 + I^- \rightarrow I_3^-$ (I^{127} resonance). The rate

constant which he reports $[(4.1 \pm 0.4) \times 10^{10} M^{-1} \text{ sec.}^{-1}$ (lower limit)] seems a little high. It exceeds the theoretical value of a diffusion controlled process by a factor of 5 to 10. Recombinations involving neutral molecules are usually somewhat slower, even if the partner is the highly mobile proton.

Among technical developments, a modified spin-echo method for measuring nuclear relaxation times described by Meiboom & Gill (89) deserves mention in addition to the description of apparatus in the above cited papers.

This survey of a very restricted recent period shows that NMR is a powerful method in the study of fast elementary reactions in solution, although the actual time range of the competing processes includes only a few decades around $\tau \simeq 10^{-3}$ sec., so far as present applications are concerned.

Perturbation methods.—A disadvantage of indirect methods lies in the difficulties often occurring in evaluation of data. Especially if more than one reaction step is involved, the analysis may become somewhat arbitrary unless the mechanism is already known. In such cases a direct recording of the course of the reaction might give more information. We shall discuss two groups of methods characterized by direct recording.

If a chemical equilibrium is subjected to perturbation by a rapid change of external parameters such as temperature, pressure, or electrical field density, the equilibration process will proceed with finite time lag and can be recorded. This is the principle of relaxation methods. In a multiple-step system the process is characterized by a whole spectrum of relaxation times, which can be expressed in terms of rate constants by well defined mathematical transformations [Meixner (90), Eigen (91)]. De Maeyer (92), Tamm (93), and Verma (94) gave comprehensive reviews on the different techniques utilizing stepwise changes of electrical field, temperature, or pressure as well as periodical oscillations of the variable (measurement of phase-shift between external and internal change: dispersion and absorption methods). Some of these techniques have been discussed in earlier reviews. Among newer developments, a temperature-jump method with spectrophotometric observation [Czerlinski & Eigen (95), Czerlinski, Diebler & Eigen (96)] and pressure-shock methods with conductometric recording [Ljunggren & Lamm (97), Strehlow & Becker (98)] are to be mentioned. The spectrophotometric method is especially suitable for chemical problems and allows the recording of small amounts of reacting substance (e.g., concentrations of 10^{-5} M and less) in the presence of a large excess of other substances (buffer, etc.). The time range between 1 sec. and a few μsec. can be covered by this technique.

The ultrasonic-relaxation techniques (93, 94) applied in recent investigations are already quite "classical." Efforts are being made to reduce the amount of liquids necessary for measurements in the lower frequency range [Andreae (99)]; in earlier investigations these sometimes exceeded 10 l. As the concentration of the dissolved substances has to be fairly high in order to allow distinction of the chemical relaxation from solvent relaxation effects, the requirement of large amounts causes a severe limitation of the method. In this respect the dispersion and absorption techniques are of some disad-

vantage compared with the specific single transient method so far as chemical relaxation is concerned. Recent success in producing sound waves up to frequencies of 10^{10} c./sec. [Boemmel & Dransfeld (100, 101)] does not include studies in liquid systems, where considerable difficulties would have to be overcome.

Relaxation methods that continuously cover the time range between 1 sec. and about 5×10^{-10} sec. are currently available. Quite a number of relaxation spectra of aqueous, multiple-step reaction systems in this time range have been studied and their reaction mechanisms have been analyzed. Recent applications range from a comprehensive study of protolytic reactions and metal-complex formation [Eigen & De Maeyer (45, 102, 103), Diebler, Czerlinski & Eigen (95, 96, 104), Wendt & Strehlow (105)] for which general mechanisms could be derived (cf. below), through the elementary redox-reactions [Diebler cf. (224)], hydrations [Ljunggren & Lamm (97)], and tautomeric changes (being carried out) to more complicated enzyme mechanisms [Alberty & Hammes (106, 107), Diebler, Eigen & Hammes (108), Czerlinski (109)]. Difficulties in earlier interpretations of sound absorption spectra in aqueous solutions of bivalent metal ions [cf. Verma (94)] were resolved by a more rigorous treatment of the coupled reaction processes, resulting in relaxation spectra [Eigen (91, 102)]. A complete analysis requires measurements in a broad frequency range unless the mechanism is already known. Studies of static influences such as application of static pressure or change of solvent dielectric constant were very helpful in clarifying mechanisms [Fisher (110), Carnevale & Litovitz (111, 112)].

Numerous applications of sound relaxation techniques to nonaqueous solutions have been reported during the last two years. Lamb (113) is continuing his excellent work on rotational isomerism. The rate of rotational transitions about the C—C, such as in the case of ethane which shows three stable configurational positions, could be measured for a number of similar substances by Lamb and co-workers (113, 114). Further results are reported by Chen & Petrauskas (115). Studies have also been made in systems such as acrolein, in which partial conjugation plays a role, in determining the energy parameters [de Groot & Lamb (116), Hall & Lamb (117)]. More extensive theoretical treatment of these phenomena was given by Davies & Lamb (118, 119). Maier (120) is continuing rate studies of association reactions involving hydrogen bonding of substances in nonpolar solvents (e.g., benzoic acid in CCl_4) using sound absorption technique [cf. Maier & Rudolf (121)]. The reactions are almost diffusion controlled; recombination rate constants lie between 10^9 and 10^{10} M^{-1} sec.$^{-1}$. Tabuchi (122) distinguishes two reaction steps when a double hydrogen bond is formed between two carboxylic groups. His extensive theoretical treatment of sound absorption (123) includes chemical transformations of any order but is only applicable to reactions proceeding in one step. Studies of association reactions in amine-water systems are also reported by Barfield & Schneider (124). It would be of interest to find out, by measurements in a larger pH-range, how far the known base dissocia-

tion may contribute to the sound absorption in this system, as found previously with NH_3-H_2O by sound absorption and dissociation field effect measurements (102).

Relaxation studies of systems far displaced from equilibrium are still very rare, though they should provide new information. Studies of water dissociation with pressure shocks exceeding 10^6 atm. in the microsecond region by David & Hamann (125) open a new field of experimental approach. Similar experiments (in the $m\mu sec.$ region) with high electric field shocks produced in a wave guide are being carried out by De Maeyer and Eigen (126).

In a certain sense the flash photolysis methods we will now discuss may also be called relaxation methods. The equilibrium usually is far displaced as the elementary process, i.e., the absorption of a light quantum or of kinetic energy from an accelerated particle, yields products, such as electronically excited states or radicals, not normally involved in the equilibrium. Among the great number of papers in this field we shall select those in which the method is used to study ordinary homogeneous kinetics coupled to the absorption of radiation. (Radiation chemistry and typical radical kinetics are reviewed elsewhere.)

An excellent survey on studies of fast homogeneous kinetics in solution by flash photolysis methods has been given recently by Porter (127). The limiting factor in time resolution is the flash duration, usually larger than 10^{-6} sec. Efforts are being made to develop more effective flash tubes: quite a number of papers in *Review of Scientific Instruments*, 1958–59, are concerned with this problem. Claesson & Lindqvist (128) [some technical data hitherto unpublished are summarized in a table in (127)] were especially successful in developing high-energy flash tubes (using capacitors up to 10^{-3} farads) that can be discharged in relatively short times, considering the high flash energies.

The flash method represents a real relaxation method for studying the ground state if a new equilibrium is established in the excited state before deactivation occurs. The back reaction of a (ground state) compound, produced via the excited state to its equilibrium concentration, can be followed. Breitschwerdt, Förster & Weller (129, 130) describe such applications to aromatic oxy-compounds.

If the products of the flash illumination are charged particles, a sensitive detection by electrometric methods is possible [Rüppel, Krog & Witt (131)]. Radical ions of triphenyl-amine in n-hexane could be identified by this and a corresponding photometric method [Witt, Moraw & Müller (132)].

Very short flash duration can be obtained using x-rays or electron beams from a linear accelerator [Burton (133), Dorfman (134)]. Burton & Dreeskamp (135, 136, 137) were able to measure directly radiation-induced luminescence decay times in the $m\mu sec.$ region using an ingenious time sampling method. They reported results for aerated benzene containing p-terphenyl as scintillator. Another method for direct measurement of fluorescence decay induced by light flashes, in the $m\mu sec.$ region, was developed by Brody (138). This technique opens new possibilities of studying directly how

energy is transferred, stabilized, and transformed in organized biological systems. Applications to the study of lifetimes of photosynthetic pigments are reported by Brody (139).

Among general applications of flash technique we may quote some examples such as the studies of reactions of semiquinones, reported by Bridge & Porter (140, 141), similar, more recent studies of aromatic ketones and ketyl radicals [Porter and Wilkinson, cf. (127)], and investigations of photo-ionization and recombination kinetics in solutions of alkali metals and aromatic negative ions as reported by Linschitz & Eloranta (142). Numerous interesting applications are concerned with biological phenomena, such as the studies of visual excitation by Abrahamson *et al.* (143) or the kinetic studies on the primary processes in photosynthesis by Witt and co-workers (144 to 148) [cf. Livingston & Pugh (149), Linschitz & Sarkanen (150), Rabinowitch (151), Amesz & Duysens (152), Lumry, Mayne & Spikes (153)]. This list of references indicates a field which, though very fascinating, is already beyond the scope of this article. Nevertheless it shows that many of the future applications of fast reaction techniques are to be expected in the field of biology.

REACTION MECHANISMS

Substitution reactions.—Interest in reactions involving the substitution of groups coupled by inorganic ions has increased as crystal field theory has become more popular with chemists. The monograph by Basolo & Pearson (154) presents an excellent survey of the whole field and will stimulate new experiments and theoretical studies. Pearson (155) in a more recent paper has reviewed his own approach to the mechanism of substitution reactions of inorganic complexes with emphasis on the implications of crystal field theory. Almost at the same time that Pearson reached his conclusions, measurements of fast substitution reactions of divalent ions in aqueous solution, including the alkaline earth metal ions Be^{+2}, Mg^{+2}, and Ca^{+2} and the transition metal ions Cu^{+2}, Ni^{+2}, Co^{+2}, and Mn^{+2}, were carried out [Eigen (91, 102)] and yielded results generally in good agreement with Pearson's assumptions about crystal field stabilization in the transition state of some of the complexes. The predominant influence in binding the water molecules in coordination spheres is of electrostatic nature. Therefore, trivalent ions such as Fe^{+3} and Al^{+3} exchange water with relative slowness, though still appreciably faster than Cr^{+3} and Co^{+3}, but almost comparable to Be^{+2} [cf. Diebler & Eigen (104), Strehlow & Wendt (105), Below, Connick & Coppel (156), Hunt & Taube (157)]. As in the case of Be^{+2}, hydrolytic processes catalyze the reaction; the rate especially depends upon the acidity of the substituting anions, in contrast to the results obtained with the other divalent ions mentioned above (102).

The results for the divalent metal ions are also supported within the orders of magnitude by recent NMR-studies of Connick & Poulson (82) [cf. Morgan & Nolle (85)], which allow estimation of lower limits of rate constants for the water exchange between coordination spheres and the bulk of

the solvent. The reported rate constants for Fe^{3+}, however, seem to be too high to fit into any one of the models suggested by the other data, and therefore should be redetermined before further conclusions are to be reached. Similar NMR-studies for paramagnetic ions in methanol solutions are reported by Pearson et al. (84).

All these measurements permit general conclusions about the mechanism of substitution of water molecules from coordination spheres of metal ions that were not obtainable by classical techniques. The relaxation measurements also allowed a separate determination of the (stepwise) substitution of outer and inner sphere water-molecules (102), the former one being generally a very rapid process with rate constants of about 10^9 sec.$^{-1}$. Conclusions from these mechanisms may be extended to interpretation of specific metal activation in enzyme reactions (108).

Among other recent studies of exchange reactions by means of more classical techniques, we have to include a report of Basolo et al. (158), stating that exchange and substitution reactions in Pt(IV) complexes are accelerated by light and Pt(II). A transfer through a bridged intermediate was suggested. Elleman, Reishus & Martin (159) report that the exchange of chloride between $[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Cl_2H_2O]^{-2}$ takes place partly by acid hydrolysis. Graziano & Harris (160) confirmed the earlier findings that the exchange of tris-oxalato-cobalt (III) with oxalate is very slow (half-time 130 hr. or more). With the corresponding Cr(III) complex, half-times were less than a day between pH 4 and 6 and at 75°C. [cf. also Long (161)]. Block & Gold (162) report that the loss of D from deuteriated hexammino cobalt (III) ions to H_2O is hydroxide catalyzed. They conclude that the acidity of the corresponding salts arises from association between the complex and a hydroxide rather than from a rapid proton transfer from amine to water.

Morris & Busch (163) studied the rates of acid "hydrolysis" of [Co(III) (HY)X]$^-$ and [Co(III) (YOH)X]$^-$, where Y is the ethylenediamine tetraacetate (EDTA) ion; YOH, the hydroxyethylenediaminetriacetate ion, and X$^-$, chloride or bromide. The net reaction for the former is expulsion of the halide, accompanied by higher coordination and loss of a proton by the organic ligand; for the latter, a water is substituted for the halide. The results indicate a unimolecular (S_N1) reaction. Illuminati & Aprile (164) report rate constants for the hydrolysis of Co(III) $(NH_3)_5$ OCOR $^{+2}$, where (OCOR) represents benzo, aceto, and trichloroaceto groups. Margerum (165) reviewed published and some unpublished work on the stability and kinetics of formation of metal EDTA complexes. Intermediate complexes with decreased coordination, or more than one metal per ligand, have been found, and a correlation between stability of the complexes with their inertness to exchange reactions is noted. Taft & Cook (166) have studied the kinetics of formation of the first complexes between metal ions and thionyltrifluoroacetone (TTA). With Sc(III), Cu(II), Zn(II), and Mg(II), the rate of TTA ionization is the rate determining step; for Fe(III), the reaction of metal ion and enol is

slower. No simple correlation of formation rates of complexes and their stability was found.

Edelson & Plane (167) report that higher quantum yields are obtained for the aquation of $Cr(NH_3)_6^{+3}$ and of $Cr(NH_3)_5H_2O^{+3}$ than for $Cr(H_2O)_6^{+3}$ (exchange with water) when irradiated with light corresponding to ligand field transitions. They attribute the difference in the former two cases to a higher energy gap between the doublet, which is the postulated reactive state, and the quartet; thermal deactivation is thus diminished. Hamm *et al.* (168) studied polarographically the rate of formation of Cr(III) complexes with acetate, glycollate, and several similar organic ions. Comparable rates were found, and a general reaction mechanism involving the dissociation of a water molecule from the complex as the slow step was postulated.

Davies & Williams (169) discuss the bromoacetate-thiosulfate and the bromopentamine Co(III)-hydroxide reactions; they conclude that, when incomplete dissociation of salts is considered, satisfactory interpretation is obtained by a two-term equation with the dependence on ionic strength required by Brønsted theory. Studies of substitution of pyridine in the inner sphere of several Pt(II) and Pt(IV) complexes are reported by Zvyagintsev & Shubochkina (170). Rates are all second order, and faster with Pt(II) than with Pt(IV). Temperature dependences are recorded.

Several studies of the exchange of oxygen between water and inorganic species have appeared. Brodskii & Vysotskaya (171) report that for anions of Groups V, VI, and VII the exchange rates were found to be greater for acids than for salts of a given anion and to decrease with the number of bound oxygens (or sulfurs); in addition, within any group the rates increased with atomic weight. An *ortho* form was postulated as an intermediate. Hoering, Ishimori & McDonald (172) found that ClO_4^- does not exchange oxygen with water during 63 days at 100°C. The rate with ClO_3^- is higher; chlorite decomposes. Between nitrous acid and water the rate was found [Bunton, Llewellyn & Stedman (173)] to be proportional to the square of the nitrous acid concentration, presumably owing to the function of N_2O_3 as an intermediate. Spitsyn *et al.* (174) report that exchange between several niobates and tantalates was complete in about 5 hr. at 95°C. According to Katz & Lapteva (175), oxygen exchange between water and CO_2 is independent of pressure and faster for H_2O than for D_2O. The exchange is complete in about 3 hr. at 90°C. and 20 hr. at 12.5°C. Martin (176) found that the half-time for exchange of hydrogen bonded directly to phosphorus in phosphorous acid was about 200 min. at 25°C. Exchanges between bromide and chloride and the corresponding hypohalites have been studied by Anbar *et al.* (177, 177a).

A number of investigations of exchange reactions in nonaqueous media have also been reported. Norris (178, 179) reviews exchange reactions in liquid SO_2; these seem to require some modification of the solvent acid-base model advocated by some for this system. With Burge (179), he finds that sulfur exchange between thionyl chloride and solvent SO_2, which nor-

mally takes place with a half-time of the order of a year, is catalyzed by $SbCl_5$, presumably acting as an acid. Rates with acid catalysis are, however, a factor of 100 less than with basic catalysis, and the presence of $SbCl_5$ inhibits the action of the basic catalyst tetramethyl ammonium chloride (and vice versa). Huston (180) lists a number of solvent systems for which the solvent acid-base formulation is adequate. He reports oxygen exchange data for SO_2 in concentrated H_2SO_4 [cf. (178)], in which SO_2 acts as a Lewis acid in the water excess region and as a base when SO_3 is in excess. Gutmann (181) also discusses acid-base phenomena in nonaqueous media. A parallel was noted by Shatenshtein & Izrailevich (182) between the deuterium exchange rates of deuterated ammonia (solvent) with solutes toluene, ethyl benzene, or similar compounds, and the formation of alkylbenzene metal derivatives.

Numerous studies of exchanges involving organic molecules have been reported. Exchange reactions between gaseous H_2 and alcoholic groups (183), of the D–H exchange in phenyl and its ethers, diphenyl amines, etc. (184, 185), of deuterium exchange in polypeptides (186), between chloroform and heavy water (187), between chloroform and chloride (188), of alkyl iodides (189, 189a), of sulfur in salts of organic thiosulfonic acids (190), and of aromatic compounds and aqueous solutions of acids (191) have been treated. A correlation between the acid-catalyzed oxygen exchange and racemization of 4-methoxydiphenyl methanol led Bunton, Llewellyn & Wilson (192) to suggest a common slow step involving the conjugate alcohol ROH^+_2. Rittenberg & Graff (193) compared the rate of mutarotation and oxygen exchange of glucose. The rate of chlorine substitution by hydroxy groups with *cis* and *trans* chlorocrotonic acids (194) was found to proceed with the same activation energy, but with a tenfold lower coefficient for the *cis* than for the *trans*. Feldman *et al.* (195) report 1 per cent isotope enrichments of O^{18} in reactions catalyzed by enzymes. A study of the H/D isotope effect was carried out by Brown & Garnett (196) by comparing the amount of tritium after recoil labelling of isopropylbenzoate in the ordinary and in the deuterated compound.

Solvolysis.—The solvent molecules often are important partners in chemical reactions between dissolved species. Predominant attention has been accorded aqueous systems and organic solutes. Elementary processes such as proton transfer and hydrolysis studied by the fast reaction technique have been analyzed by some of the authors mentioned above.

The most simple example is provided by an aqueous solution of a single weak acid or base. Even in these systems three reaction steps have to be distinguished (102): the simple dissociation of the acid or base, the normal water dissociation equilibrium, and the direct reaction between water and the acid-anion or the base-cation (hydrolysis). Since the kinetics of neutralization in pure water (45) is known, kinetic measurements with corresponding acid or base solution permit complete evaluation of the kinetics involved. Direct recombinations of protons or hydroxyl ions with counter ions (e.g., acid anion or base cation respectively) are usually diffusion controlled if hydrogen bond-

ing with solvent structure allows unhindered proton jumping [the rate of which has been measured in ice crystals (45)]. Real exceptions from this rule are not known. Where they have been reported, either formation of inner hydrogen bonds (55, 102) or inner molecular rearrangements (as pseudoacids, dehydrated molecules, etc.) prevent unhindered exchange [cf. (8, 22, 32, 34)], or the method applied was inadequate with respect to evaluation of the data in terms of homogeneous rates [cf. (35)]. The rate constants of diffusion controlled protolytic reactions lie usually in the range of 10^{10}–10^{11} M^{-1} sec.$^{-1}$ (34, 38, 39, 45, 55, 58, 102); they may be smaller when the partners carry electric charges of the same sign (95).

The transfer of a proton between an acid and a base, even between identical particles (an acid and its anion) usually also is a very rapid process (55, 58, 72, 73, 74, 108). If the partner is a better proton acceptor, the reaction most frequently is diffusion controlled. However, there seems to be a slight hindrance for proton transfer in H-bonds of the type N . . . $^{+}$H–N (55, 58, 72, 73, 74). Hydrolytic polymerizations (e.g., 2 $BeOH^{+} \rightleftharpoons (BeOH)_2^{+2}$) usually are much slower processes than the first step in hydrolysis ($Be^{+2} + H_2O \rightleftharpoons BeOH^{+} + H^{+}$) though they sometimes still lie in the range of applicability of the techniques discussed in the first section [cf. Diebler & Eigen (104)].

The general mechanism of the protolytic reactions seems to be quite well understood, though it should be confirmed by a larger number of examples. Solvolytic reactions involving tautomeric changes can be much slower (cf. above), especially if inner molecular rearrangements are involved. Classical techniques can often be applied to follow the overall reaction in such cases. Attention has to be paid, in the selection of experimental conditions, to the fact that these processes are most commonly acid or base catalyzed.

Hansen (197) studied the cleavage of 2-dimethylaminoethylthiol propionate by use of an automatic titrator to keep the pH constant and to record simultaneously the addition of acid necessary to do so. The procedure affords the simplicity in interpretation of studies in buffered systems, without the interferences sometimes introduced by the buffers.

Svirbely & Weisberg (198, 199) analyze the alkaline hydrolysis of 1, 3, 5 tris (4-carbomethoxyphenyl) benzene as a three-step reaction. According to Pritchard & Long (200) the acid catalyzed hydrolysis of trimethylene oxide (studied in H_2O, D_2O, and 40 per cent aqueous dioxane) proceeds by formation of a conjugate acid, followed by a rate-determining rearrangement to a carbonium ion. Euranto (201) studied both the hydrogen ion catalyzed and the uncatalyzed hydrolysis of chloromethyl esters of formic through n-butyric acid, as well as acetates of other halide substituted alcohols, over a range of temperature, and with variations of solvent. Tommila, Takenen & Salonen (202) observed that in the basic hydrolysis of ethyl oxalate, both activation energy and frequency factor increase with fraction of acetone or ethyl alcohol in the solvent, but in the case of ethyl malonate these factors pass through a minimum.

Ketelaar & Gersmann (203) correlate the rates of alkaline hydrolysis of

some phosphoric acid esters, which are significant in insecticide chemistry, with their activity as enzyme inhibitors. Selim & Leduc (204) found that hydrolysis of dimethyl and monomethyl phosphate at 100° is first order and pH dependent. Holbrook & Ouellet (205) found for the nonenzymatic hydrolysis of p-nitrophenyl phosphate a dependence of rate on pH, and at pH 2.6, an activation energy of ca. 26 kcal./mole and entropy of -14 e.u. Pozin, Kopylev & Zhil'tsova (206) studied the hydrolysis of $Ca(H_2PO_4)_2$ phosphate in aqueous solution, and Osterheld (207) studied the kinetics of aqueous reversion of $Na_4P_2O_7$. Emschwiller (208) reports that ruthenocyanides decompose in aqueous solution to form pentacyano compounds.

The reactions of alkyl bromides in ethanol plus 1 to 24 per cent water have been studied by Clement & Rice (209). Koskikallio (210) reports on the base catalyzed reaction of acetic anhydride with methanol-water solvent. Pyridine catalyzed methanolysis was accelerated by addition of water. Solvolytic reactions of R_3SnCl and R_3SiCl, where R indicates an organic radical, were investigated by Prince (211). Rapid alcoholysis and hydrolysis, as well as pronounced steric effects, were found.

Jullien et $al.$ (212, 213) report studies of the hydrolysis of several chlorohydrins, mostly cyclic. In their proposed mechanism, the departure of the Cl in the rate-determining step is assisted by a molecular rearrangement to a ketone. Tertiary chlorides are too mobile for this mechanism to contribute. Ballinger & Long (214) investigated the kinetics of base catalyzed hydrolysis of 2-chloroethanol and 2-chloropropanol (to form epoxides) in H_2O and D_2O. Equilibrium constants for the ionization (first step of the reaction) of the alcoholic H or D of the ethanol compound are given. The faster rates were found in D_2O, contrary to the usual finding; a decrease in solvation in the transition state is offered as an explanation. Possibilities for distinguishing between different mechanisms for base catalyzed reactions by study in H_2O and D_2O media were discussed. In another report concerning the hydrolysis of 2-chloroethanol in H_2O and D_2O, Swain, Ketley & Bader (215) conclude that the 2-chloroethoxide ion is indeed an intermediate in the formation of ethylene oxide. Kempa & Lee (216) found the rates of alkaline hydrolysis for ethylene carbonate somewhat faster than for propylene carbonate, and both were many orders of magnitude faster than in water. The hydrolysis of isopropoxy-methyl-phosphoryl chloride was used by Larsson (217) to illustrate the study of kinetics with the use of distribution between two phases (one of the reactants reacts with the material in one of the phases). A research program on the acid and alkaline hydrolysis of chlorinated methanes is completed with a report (218) of Fells & Moelwyn-Hughes on results with $CHCl_3$ and CCl_4. All observations are discussed in light of theoretical models.

$Oxidation$-$reduction$ $reactions$.—Studies of the kinetics of reactions involving only an exchange of electrons between identical particles offer an excellent possibility for an interpretation of mechanisms that avoids all complications stemming from differences in affinities.

Taube (219), in a review of redox reactions of metal ions, divides processes with relatively well established mechanisms into two classes. In one, usually fast, the first coordination spheres of the reactants are not changed in the activated complex [e.g., ferric, chromic, or cobaltic complexes, cf. also Zwickel & Taube (220)], though they may be distorted; in the other, a bridge is formed by a ligand between the partners. The latter can be established at present only in oxidation-reduction reactions between different elements, and in reactions where the reactant of one element and the product of the other have coordination spheres of low lability. The mechanism presumably applies to exchange reactions as well. Different bridging elements give interesting differences in rates, including a pronounced increase in cases having a conjugated system of double bonds between the partners [cf. Fraser, Sebera & Taube (221, 222)].

The most appropriate method for studying fast electron exchange is the electron spin resonance technique. Recent applications by Weissman (68) and co-workers involve the systems naphthalene negative ion—naphthalene (69) and sodium benzophenone—ketylbenzophenone (223). Second order rate constants as high as 10^7 to 10^9 M^{-1} sec.$^{-1}$ could be estimated for the electron exchange in the naphthalene system. In the other case the results indicated that the exchange process involves a sodium atom rather than a simple electron transfer only.

Also, the temperature relaxation technique [cf. (92, 95, 96)] proved suitable for studies of very fast electron transfer processes between different partners, as has been shown by Diebler (224) using the system $Fe(CN)_6^{-4}$—$Fe(CN)_6^{-3}$-dichlorophenol—indophenol (redox indicator). The second order rate constant for the first (rate limiting) electron transfer from $Fe(CN)_6^{-4}$ to the indicator has been found to be $1.5 \cdot 10^5$ M^{-1} sec.$^{-1}$.

Wahl and co-workers (225 to 228) report studies of electron exchange between complexes having the same structure and differing in charge by only one unit. Franck-Condon restrictions in such cases are presumably less important. A review given by Wahl (229) includes the systems MnO_4^{-2}—MnO_4^{-1}, $Fe(CN)_6^{-4}$—$Fe(CN)_6^{-3}$, $Fe(C_5H_5)_2$—$Fe(C_5H_5)_2^+$, $Fe(phen)_3^{+2}$—$Fe(phen)_3^{+3}$ and $Os(dipy)_3^{+2}$—$Os(dipy)_3^{+3}$ [phen = 1, 10 phenanthroline; dipy = 2,2'-dipyridyl]. The reactions are in general very fast; second order rate constants estimated to be $> 10^5$ M^{-1} sec.$^{-1}$ (e.g., between ferric and ferrous phenanthroline complex) were found by Hartridge-Roughton mixing techniques, followed by fast separations. Comparison of the results with the (R.J.) Marcus, Zwolinski & Eyring (230) eléctron tunnelling theory and the (R.A.) Marcus (231) configuration theory were not good in a quantitative sense, although there was some correlation. This is perhaps not surprising, because of the approximate nature of the models. Further, specific effects for different cations indicate that bridging mechanisms may also be important here in overcoming coulombic repulsion between exchanging species (229). Laidler (232) has modified these theories somewhat in a discussion of the

$Fe^{+2,+3}$ exchange. On the basis of a diffusion controlled mechanism hindered by electrostatic repulsion and followed by tunnelling of the electron when the optimum distance is attained, he reports a computed $\Delta F\ddagger$ of 15.4 kcal/mole, compared with the experimental of 16.8 Krishnamurty & Wahl (233) report results on the exchange of V(II)–V(III); in 1 M HClO₄, the exchange was second order and half-times were of the order of a few minutes. Lowering the acidity or introducing chloride increased the rate, presumably by providing a hydroxyl or chloride bridge. A complex mechanism for the Sb(III)–Sb(V) exchange in 3 M HCl with added bromide is discussed by Turco (234).

If more formidable rearrangements are necessary, reactions can be quite slow. Appelman, Anbar & Taube (235) report that exchange between Co(II) and aquo-pentammine Co(III) went less than 0.4 per cent to completion after a week at 45° in acid solution. In ammoniacal media, rates are faster.

Baker, Basolo & Neumann (236) report studies of electron exchange of tris (1–10 phenanthroline) complexes of Co(II) and (III) and also the 2–2' bipyridine and 2,2'2'' tripyridine complexes. Rates for concentrations in the region 10^{-4} M of the reactants are of the order of 10^{-6} M min.$^{-1}$. Some rather small specific anion effects were observed, and ion pairs with chloride were postulated. Changing from water to D_2O as solvent had little effect, while water-acetone solutions showed some shift. The correlation with predictions of various models is not very satisfactory. Cattrall, McKellar & West (237) also discuss exchanges between cobalt complexes.

Newton & Rabideau (238) review exchange reactions involving U, Np, and Pu, as well as other oxidation-reduction reactions of these elements. There are pronounced differences in rates between water and D_2O media; presumably hydrogen atom transfers are involved. Indelli & Amis (239) determined the activation energy for the U(IV)–U(VI) electron exchange reaction in water-ethanol, which decreases with increasing alcohol concentration.

Halpern (240) compares the rates of reactions between 1- and 2-equivalent oxidizing and reducing agents with electron exchange rates of the reactants, and concludes that the principle of equivalent exchange, which predicts these should be slow, has only limited applicability. Other papers by this author include the kinetics of the permanganate oxidation of formic acid and formate in aqueous solution [Taylor & Halpern (241)], the kinetics of oxidation of U(IV) by Tl(III) [Harkness & Halpern (242)], and the catalytic activation of molecular hydrogen by metal salts [Chalk & Halpern (243, 244, 245)].

Fast (reversible) redox reactions initiated by light quanta can be followed by suitable (stationary and nonstationary) photochemical methods. Ainsworth (246) discussed the kinetics of the photoreduction of thionine by ferrous ions, where the electron transfer occurs between the excited species of thionine and the ferrous ion. His data suggest some modification of the mechanisms proposed by Rabinowitch (247), Hardwick (248), and Schlag

(249). Measurements of the quenching of the thionine fluorescence by ferrous ions [Havemann *et al.* (250, 251, 252)] seem to support some of the assumptions regarding complex formation between Fe^{2+} and thionine. Similar studies involving the methylene blue system are reported by Parker (253, 254).

Oxidation-reduction reactions involving more than one element, though more complicated than those involving simply an exchange of electrons between isotopes, are generally of more practical interest. The heaviest elements continue to receive much attention. In a study of reactions between Pu(VI) and U(IV), Newton (238, 255) related his results to earlier measurements on Np(IV)–Np(VI) and Pu(IV)–Pu(VI). He concludes from acid dependence that two consecutive activated complexes, which are hydrolytic copolymers of the two elements, are involved [(cf. Newton (256)]. Zielen *et al.* (257) derive an expression for the kinetics of the reduction of Np(VI) by H_2O_2, which fits data obtained over a range of temperature, ionic strength, and acidity. Hindman, Sullivan & Cohen (258) report that the presence of deuterium slows reactions involving Np(IV), (V), and (VI), in perchlorate and sulfate media by as much as a factor of 5 in the rate constant. Siddall & Dukes (259) conclude that in HNO_2 catalyzed oxidation of Np(V) by nitric acid, the slow step is the reaction of NpO_2^+ with protons to form an activated complex, followed by a fast oxidation of the neptunium by HNO_2 and regeneration of nitrous acid from the products. Iwamoto (260) reports rate constants for disproportionation of UO_2^+ obtained by potential measurements at constant current. Kinetics of the reaction between Pu(VI) and Tl(III) is analyzed by Rabideau & Kline (261).

With respect to higher rows in the periodic table, Johnson & Martin (262) report that the oxidation of Ce(III) by concentrated HNO_3 at 90–110° is reversible. They postulate an electron transfer between cerium and NO_2^+, first order in each reactant, with a $\Delta H\ddagger$ of 8 kcal/mole. Cristau (263) reports differences in times of the order of days in the reduction of different compounds of As(III) by hypophosphorus acid in the presence of bromide. Oxidation of Fe(II) [Czapski & Stein (264), Davis, Gordon & Hart (265)] and of I^- [Czapski, Jortner & Stein (266)] has been effected by the introduction of atomic hydrogen into acidic solutions of the ions. Freund (267) proposes a mechanism for the reduction of ferricyanide by borohydride to account for the observations that it is first order in BH_4^- and H^+ concentration and independent of ferricyanide. Chertkov (268) reports the effects of temperature, oxygen pressure, inhibitors, and reaction products in the oxidation of sulfite. Harrison & Thode (269) found that sulfate with S^{32} was reduced 2.2 per cent faster by HI, hypophosphorus acid, and HCl than with S^{34}. This agrees with the Biegeleisen mechanism, with an S—O bond-breakage rate controlling. In a polarographic study of the oxidation of chloride, Tedoradze (270) found that ClO_3^- is formed at low Cl^- concentrations, but that the yield drops off sharply above 0.006 M HCl. Carassiti & Dejak

(271) investigated the effect of the presence of several different anions and cations on the $I^- - S_2O_8^{-2}$ reaction and found that cations had the most pronounced effects. Rate constants and activation energies were obtained for reactions of hydroxylamine-N-sulfonates [e.g., $NH(OH)SO_3^-$ and $N((OH)(SO_3)_2^=$] with bisulfite by Seel *et al.* (272). Studies of the Van Slyk reaction (ammonia and nitrous acid to produce N_2) have been carried out by Bauer *et al.* (273, 274); the interpretation is not completely clear. Gupta & Ghosh (275) report on the effects of acidity and Mn^{+2} on the rates of reduction of permanganate. Duke (276) has reviewed a number of oxidation-reduction reactions of inorganic species; he postulates that generally they are preceded by, or simultaneous with, a reaction between a Lewis acid and base.

There has been the usual large output of studies concerning oxidation-reduction reactions of organic substances, and we shall mention briefly a number of these. Malinowski & Levitt (277) find the oxidation of isopropyl alcohol by $K_2S_2O_8$ first order with respect to the oxidizing agent. Ogata & Tabushi (278) studied the kinetics of oxidation of dimethylanilines substituted in the *para* position; the rates of oxidation in acid media were proportional to the electron withdrawing power of the substituent (vice versa in alkali) as indicated by the acid constants. In a polarographic study of the oxidation of semicarbazide in EtOH, Trandafirescu (279) attributes an increase in diffusion current with time (up to three days) and a change in half-wave potential to a slow reaction with the solvent. According to Pryor (280), the slow step in the oxidation of *m*-toluic acid to isophthalic acid by aqueous sulfur solutions is probably the extraction of a benzyl H atom by a polysulfide.

Chatterji *et al.* (281, 282), in reports concerning the oxidation of propyl alcohol and capryl alcohol by chromate, discuss the effects of concentration, substituents, temperature, and negative catalysts. Anantakrishnan & Venkatasubranian (283) find the chromate oxidation of isopropyl alcohol and cyclohexanol in acetone to be first order. Other much encountered organic oxidations whose mechanisms have received attention are those by periodate [Shiner & Wasmuth (284)], and the oxidations of ether [Debiais *et al.* (285)].

Kaplan (286) reports that ethanol and acetaldehyde are oxidized more slowly by bromide on a deuterated than on a protonated molecule. Edwards *et al.* (287) present results on the kinetics of aniline nitrosation and of the glycoltellurate reaction; the general framework of the discussion involves a postulated deoxygenation of an oxyanion (change in coordination number), which occurs before or during the rate determining step.

Milburn & Taube (288) describe tracer experiments designed to clarify the kinetics of the oxidation of oxalic acid. No exchange of oxalate oxygen with solvent or oxidizing agent was found with oxidation by Ce(IV) or hypochlorous acid, but some exchange was found with H_2O_2. No exchange between $C_2O_4^{-2}$ and CO_2 was induced in oxidation by Mn(III).

Miscellaneous reactions.—Space limitations make it impossible to include a discussion of many interesting studies that have appeared during the period in question. In order to provide a more extensive bibliography, we list references 289 to 314, which deal with reaction kinetics of inorganic solutions, and 315 to 352, which concern organic reactions.

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VIBRATION-ROTATION SPECTROSCOPY[1]

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During recent years reviewers of vibrational spectroscopy in this series have commented with monotonous regularity on the large number of papers appearing in this field. The majority are applications of spectral measurements to specific compounds and since the results may be found through Chemical Abstracts they do not require separate listing in a review. The great majority of the more fundamental papers are to be found in the *Journal of Chemical Physics* or *Spectrochimica Acta* and the newer publications, the *Journal of Molecular Spectroscopy* and *Optika and Spektroskopiya*. The latter journal, published in Russia, is now translated under the auspices of the Optical Society of America and appears in English as *Optics and Spectroscopy*.

Many of these applications are made by workers who are interested in the compounds rather than in the techniques; they expect to be served with the fundamental and theoretical background from specialist papers, textbooks, and colleagues. It is appropriate this year to take stock of this knowledge especially in relation to force constants and judge its sufficiency against general requirements. When the reviewer accepted the task of writing this review for the 1960 volume, he intended to include a large section on infrared intensities. However this subject has been comprehensively reviewed by Mills (1) during the year and it is unnecessary to duplicate his material. In writing his review Mills had access to a number of reports, advance copies of papers, etc., and his review includes some new material.

FORCE CONSTANT TREATMENTS

The well known works of Herzberg (2) cover the groundwork of the vibration spectroscopy very fully. They have stood the test of time extremely well and it is unfortunate that Professor Herzberg's active research interests have not left him time to complete the trilogy. These books have also been standard works for many items of terminology and the few gaps were filled by the recent recommendations of Mulliken (3), which have been widely accepted. Another useful book is *Molecular Vibrations*, which deals especially with force constant problems (4). Any student can set up a vibrational problem for himself with these guides and discuss the symmetry properties, selection rules, and frequencies when provided with the molecular geometry and a force field. For larger molecules this can be a tedious task and electronic computers can be called in to help. There are also some advantages (5) to working in Cartesian, as opposed to valency, symmetry coordinates. The reverse problem, that of calculating force con-

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[1] The survey of literature was concluded November 1959.

stants from the frequencies, is much more troublesome and not normally susceptible to a unique solution. The difficult part of this task is in deciding what assumptions can be made. Provided with the assumptions and an approximately correct force field, a computer can refine the field so as to give a best fit with the observed frequencies; if the frequencies are equal in number to the disposable constants of the force field, the fit may be adjusted exactly. Unfortunately, this does not ensure the correctness of the assumed force field.

In the simple case of symmetrical non-linear triatomic molecules (6), e.g., H_2O, the symmetrical stretching and the bending frequencies are in the same class and are controlled by three harmonic force constants. These are usually taken as a bond stretching, an angle deformation, and an interaction constant. When two frequencies are known it is possible to plot a graph with two of the force constants as ordinate and abscissa and the third as a running parameter. Such a curve is commonly an ellipse and serves to indicate upper and lower bounds for each force constant. Attempts to solve the equations with values outside this range lead to imaginary values for the other constants. If an isotopic molecule is available, two more experimental frequencies will be known from experiments and a second ellipse can be drawn. Points of intersection of the two ellipses represent alternative exact solutions of the problem. Intuition and analogy with related molecules may serve to distinguish the true from the false solution. It is, of course, necessary to fulfill the Redlich-Teller product rule if self-consistent solutions are to be obtained.

The procedure outlined in the last paragraph represents a formal answer to the problem of determining force constants from the observed frequencies, but, in practice, the procedure is unsatisfactory. Normally the two ellipses are nearly coincident and so are almost parallel at their point of intersection. This means that the accuracy of determination of the points of intersection is low and very sensitive to experimental errors, corrections for anharmonicity, adjustments to fit the product rule, shift of fundamental frequencies by interactions with combination bands (Fermi resonance), etc. As a practical procedure it is far from satisfactory for deuterated molecules and worse for other isotopic substitutions, and with more than two frequencies in a symmetry class, the procedure is even less favourable.

As a result, investigators have turned to other sources of information about force constants. The most useful appears to be Coriolis coupling. The theory of this has been given in a general case by Meal & Polo (7, 8, 9). Again there are relationships—some of which depend on isotopic masses—that are independent of force constants and also independent of the relationships between these force constants and the observed ζ value. The number of molecules for which accurate and reliable ζ values are known is small, but with the advent of very high resolution spectrographs this may soon be increased.

Information is also to be obtained from centrifugal distortion constants (10). These may be obtained from well resolved rotational fine structure or, more accurately, from microwave gas spectra. The precision of the force constants appears to be good (11) but it is clear that there may be hidden errors. Verdier & Wilson (12) find that the equations for the force constants for the molecule N_2O lead to imaginary solutions, whereas the equations for the molecule OCS gave good agreement with those obtained from an isotopic frequency method. However, the interaction constant, 1.252 mD/A, for C=O and C=S differs appreciably from the value 0.96 ± 0.01 mD/A (11) obtained independently by a similar method using slightly different bond lengths. Unfortunately it appears that distortion coefficients are not as valuable as had been hoped.

One further possibility is to obtain information from the vibrational amplitudes (13) as determined by electron or x-ray diffraction. Here again the applications are likely to be inaccurate and it is more likely that force constants will be used to determine the amplitudes (14, 15, 16).

In the absence of knowledge of the correct force fields one is reduced to choosing a field which seems inherently likely on grounds of molecular structure. There are many and various assumptions that may be used to reduce the number of force constants to no more than the number of independent frequencies to be fitted. The most common assumption is a valency force field. This system introduces simple quadratic force constants for the separation of atoms that are joined directly by a bond in the normal chemical structure. In addition all angles subtended by two bonds joined to one atom merit a bending constant. In the simplest form, interaction constants are omitted except for those that are inescapably introduced through redundancy conditions (17, 18). Such a field usually contains too few constants to be capable of rendering accurate values of the fundamental frequencies and consequently, interaction constants are introduced. This is often done on an *ad hoc* basis, especially since small constants may occasionally lead to quite large frequency changes. Standard procedures for introducing interaction constants in an apparently less arbitrary manner (19) have not been widely used. Closely spaced frequencies are more affected by such interactions than those that are widely separated from others in the symmetry class; e.g., C—H stretching.

When large interaction constants are introduced it is often possible to see the chemical features to which they correspond. One important type of interaction omitted in the simple valency field is the van der Waals repulsions between indirectly bonded atoms; these are included specifically in the Urey-Bradley (20, 21) field. Another approach is to consider likely changes of electronic structure on deformation. For example, carbon dioxide can be considered as compounded from three valence-bond structures: viz.

$$O=C=O, \; I; \quad O^-\!-C\equiv O^+, \; II; \quad O^+\equiv C-O^-, \; III.$$
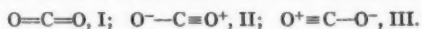
If the left hand carbon to oxygen link is stretched and that on the right hand contracted, then the structure tends to that of form II, and the deformation $(\Delta r_1 = -\Delta r_2)$ is more favourable than a deformation of the same total magnitude in which both links are stretched equally, $(\Delta r_1 = +\Delta r_2)$. The energy contribution $k_{12} \Delta r_1 \Delta r_2$ should therefore be lower in the first instance, which implies that k_{12} should be a positive quantity as is indeed observed. There are more sophisticated arguments in other cases, especially those relating to change of bond direction. These have been discussed by Linnett and his colleagues (22) and the constants are referred to as *orbital following constants*. The arguments are available to justify the introduction of particular constants but have not yet reached the state where a clear and unequivocal set of rules can be invoked.

There are obviously many ways of treating the information to obtain satisfactory force fields and the choice of method in any instance depends on the proclivities of the investigator and also on the extent of experimental data available. Table I shows the way in which authors publishing in 1958 and 1959 have, in fact, undertaken force constant treatment. The columns show: (i) molecules, including isotopic species used; (ii) the number of *independent* harmonic constants employed; (iii) the number of such constants required for an exact description of a general field of the required symmetry; (iv) the number of known frequencies; (v) the average deviation between calculated and observed frequencies, this has been preferred to a root mean square deviation which unduly weights one bad agreement that may be due to a mis-assignment; (vi) comment on the type of field used; and (vii) reference.

There are several cases in this table in which the same molecules have been discussed independently. For MoF_6, WF_6, and UF_6, Linnett & Simpson (38) had seen an advance copy of Claassen's work (37) on the same molecules before their own work was fully written up and therefore they discussed the differences. The two treatments are very similar but differ in the assumption that is made regarding interaction constants needed to reduce the F_{1u} class from three to two independent constants so that they are thereafter determined by fitting the two observed frequencies. Linnett and Simpson discuss several restrictive assumptions and Table II lists the permitted ranges for the X—F stretching-force constant when all restrictions are applied. These are compared with Claassen's values and it can be seen that in this case the principal constants, at least, can be obtained with 5 to 10 per cent precision, using different well chosen assumptions. Claassen has also shown that the Urey-Bradley field (65) leads to negative values of the angle-bending constant and is therefore insufficient in this instance.

The various calculations for the boron halides differ chiefly in the exact assignments made, but a more interesting variation exists between the force fields for the CrO_4'' ion obtained by Stammreich, Bassi & Sala (29). The principal Cr—O stretching-force constant is 6.76 mD/A if interaction between Cr—O stretchings is neglected, but only 5.48 mD/A if interaction be-

TABLE I

FORCE CONSTANT TREATMENTS IN 1958–9

(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)
$COCl_3$, $COClBr$ etc.		1	1	exact	Out-of-plane only	(23)
P_4	3	1	3	exact	Adjusted for anharmonicity	(24)
BF_3, BCl_3, BBr_3, BI_3 using ^{10}B and ^{11}B	4 each	5 each	4 each	exact	Various fields compared	(25)
Planar XY_3 e.g., BF_3, CO_3^- etc.	4 each	5 each	4 each	exact	Adjustment for anharmonicity OVFF assumption	(26, 27)
Tetrahedral XY_4 molecules, e.g. SiF_4, SO_4^- etc., CdI_4^- etc.	4 each	5 each	4 each	exact	Two different force fields used	(28)
CrO_4''	4	5	4	exact	Zero-order frequencies used	(29)
CH_4, CD_4, CT_4	5	5	10	0.3 cm^{-1}	Zeta values satisfactory	(30)
$GaBr_4''$, $InBr_4''$, $TlBr_4''$, $CdBr_4''$	—	5 each	4 each	exact	Ranges quoted for force constants	(31)
$POBr_3$, $PSBr_3$	5	12 each	6 each	exact	Ranges quoted for force constant	(32)
$^{10}BH_4$, $^{11}BH_4$, BD_4, $^{11}BD_4$	6	5	14	5 cm^{-1}	—	(33)
NF_3	6	6	4	exact	Uses Dj	(34)
$^{12}C_2N_2$, $^{13}C^{13}CN_2$	6	6	10	1 cm^{-1}	—	(35)
$CH{=}CHBr$ and deuterated species	6 each	6	24	2 cm^{-1}	Out-of-plane only	(36)
SiH_3I, SiD_3I	6 each	12	6+6	8 cm^{-1} (SiD$_3$I)	SiH$_3$I fitted exactly	(37)
MoF_6, WF_6, ReF_6, NpF_6, OsF_6, IrF_6, PtF_6, UF_6, PuF_6	8	7 each	6 each	exact	—	(38)
SF_6, SeF_6, TeF_6, MoF_6, WF_6, UF_6	9	7 each	6 each	exact	Urey-Bradley	(39)
$Fe(CO)_5$	8	48	18	15 cm^{-1}	—	(40)
S_n	9	17	20	8 cm^{-1}	—	(41)
$Cu(CN)_4^=$	9	17	11	good fit	—	(42)
$CH{=}CH{-}CH{=}CH_2$ trans.	9	16	6	56 cm^{-1}	Out-of-plane only, force constants transferred	(43)
$Ni(CO)_4$	11	17	9	exact	—	(44)
$Ni(CO)_4$	8	17	9	good	—	(45)
CCl_4, CCl_3Br, CCl_2Br_2, $CClBr_3$, CBr_4	12 in all	51 in all	29	4 cm^{-1}	Force constants transferred between different molecules of the set	(46)
$HCOOH$, $HCOOD$	12	28	8	30 cm^{-1}	In-plane only. High and low frequencies factorized	(47)
$CH_2{=}C{=}CH_2$	13	23	20	20 cm^{-1}	—	(48)
$C_5O_6Cl_6$	16	17	9	exact	—	(49)
$CH_2{=}CHCl$, $CH_2{=}CDCl$	20	51	23	17 cm^{-1}	—	(50)
$CHClF_2$	27	27	9	9 cm^{-1}	—	(51)
$CHClF_2$	27	27	9	11 cm^{-1}	—	(51)
CH_3SiH_3	—	37	9	5 cm^{-1}	Force constants taken from $C_2H_6SiH_6$	(52)

See also: C_4F_8 (53); C_5H_{10}, cyclopentene (54); C_5H_{10}, C_5D_{10} cyclopentane (55); $CH_3C_5H_9$, methyl cyclopentane (56); $CH_3{-}C{\equiv}N^+{-}CH_3$, (57), CHONHNHCHO, diformyl hydrazine (58); $CH_3CONHCH_3$, N-methylacetamide (58); $m\text{-}(CH_3)_2C_6H_4$, meta-Xylene (59); C_6H_6, C_6D_6, Naphthalene (60); $Cr(C_6H_6)_2$ (61); disiloxane, trisilylamine (62); $CrO_4^=$, dichromate (63); $NH_4^+SO_4^-$, sulphamic acid (64).

tween Cr—O stretching and angle bending is omitted. This is a case where one assumption is necessary to obtain a unique field from four observed frequencies. Though this change is larger than is common, it serves as a warning that the nature of the treatment of interaction constants can change a principal stretching constant by 20 per cent.

Another duplication in Table I is that of $Fe(CO)_5$; here the disagreement is considerable, extending even to the molecular symmetry and, therefore, to the frequency assignments. Murata & Kawai (39) favour the trigonal bipyramid, D_{3h}, whereas O'Dwyer (40) is unable to assign the spectrum on this basis and prefers the tetragonal pyramid, C_{4v}. The values obtained for the $C\equiv O$ stretching force constant are 16.0 (39) and 16.8 (40) and for the Fe—C stretch, 2.08 (39) and 1.62 (40) mD/A. These values are clearly no more accurate than could have been obtained by transference from $Ni(CO)_4$, where the assignment appears a little more certain and the values (44) for the stretching constants are 17.3 mD/A for $C\equiv O$ and 2.1 mD/A for Ni—C. A later calculation (45) gives these constants as 16.8 and 2.1 respectively. It is noticed that corrections for anharmonicity are very seldom applied and yet where this can be done, as in the methyl halides (66), the corrections can easily amount to 5 per cent. If Fermi resonance is important this may be an underestimate.

TABLE II

COMPARISON OF X—F FORCE CONSTANTS FROM DIFFERENT AUTHORS

Molecule	MoF$_6$	WF$_6$	UF$_6$	
X—F Force Constant				
Linnett-Simpson (38)	4.84–5.07	5.08–5.25	3.68–3.78	mD/A
Claassen (37)	4.73	5.13	3.80	mD/A

Although Table I refers only to the work of the years 1958 and 1959, extension to the work of earlier years would not have greatly altered its character. In particular, there is wide diversity in the treatments required to reduce the number of force constants to no more than the observables. The present position has yet to be reviewed generally and have its adequacy assessed against present and future needs; such an assessment necessarily reflects only the individual reviewer's personal opinion. Force constant treatments are required for a variety of reasons. First, a table of typical force constants are required for transference to new molecules and then for use in calculating fundamental frequencies. At best this is a rough guide only, but such a calculation can be of great value, especially when closely related molecules have not been assigned, as in the case of hexafluorobenzene (67). For this purpose the present values of force constants are sufficiently accurate,

particularly since most treatments are based on closely related molecules. Useful tables of force constants are to be found in (2) p. 193, (4) p. 175–6, and (68) p. 85. Agreement with observations to 40 cm.$^{-1}$ is helpful, and it is unlikely that better will be obtained for molecules of moderate complexity (8 to 20 atoms) unless the molecule from which force constants are transferred is very similar. In such a case, assignment by means of a characteristic frequency style of argument is usually preferable.

Second, force constants are used in Badger's rule or its variants (69 to 73), that relate these constants to bond distances, electronegativities, position in the periodic table, etc. While there are clearly some trends to be observed and empirical correlations over restricted ranges certainly exist, bond distances derived from force constants, especially in polyatomic molecules, are not normally considered reliable. They are, for instance, omitted in the standard bibliography, *Interatomic Distances* (73a).

Third, force constants, especially interaction constants, can be used to suggest features of the electron distribution and its behaviour under distortion as outlined for CO_2 above. Quite ingenious arguments are used to justify the signs or the large magnitudes of interaction constants, especially those involving angle bending (22). Although many of these explanations are probably correct, the force fields are not always sufficiently certain and it is difficult to allow for all interactions. As a consequence, when precise assumptions are made, absurdities such as negative or imaginary principal force constants often arise even though the assumptions are not unreasonable.

When relating valency force constants to properties, using the method sketched in the last paragraphs, it is not always remembered that force fields resemble dipole moments, energies, polarizabilities, etc., in that they are a property of the entire molecule and inherently incapable of being uniquely subdivided into a set of constants pertaining severally to individual bonds, angles, or pairs of these. Any such division is artificially made by those discussing the problem and may be made in more than one way especially when there are redundancy conditions between valency coordinates.

Fourth, molecular force fields are useful for the calculation of normal coordinates. Approximate coordinates are often quoted in diagram form for general interest, but their important uses require exact forms. This is especially true for the interpretation of infrared (1) and Raman intensities. Good values are also required for the discussion of vibronic transitions in the ultraviolet, particularly where the purely electronic transition (i.e., the 0—0 band) is forbidden. It is quite clear that sufficiently accurate force fields are not yet known for many molecules and that this lack is hindering advance in this field. At present the experimental intensity measurements are not of the highest accuracy but the difficulties are being removed quite rapidly. It is certainly desirable that, where possible, improved force-fields should be made available which correctly predict the frequencies corrected for anharmonicity, the Coriolis coupling parameters, and the centrifugal distortion

constants for all isotopic species. A fuller treatment of the errors in dipole moment or polarizability gradients that arise from force field errors is also required. Existing discussions that relate to SiF_4, $SF_6 \cdot CF_4$ (74), and to PH_3 (75) suggest that errors may be very large.

A final reason for requiring force fields is for comparison with theoretical quantities derived from electronic wave functions. For polyatomic molecules this is a requirement for the future, in as much as force constants are difficult to derive with accuracy because they are often obtained theoretically as a small difference between two large quantities. Nevertheless, with the wide-spread use of computers it is likely that this problem will be successfully tackled.

ISOTOPIC RULES

For the full assignment and calculation of force constants, considerable use is made of isotopic substitution, mainly by deuterium. Consequently the theory of the changes to be expected on isotopic substitution has been more thoroughly investigated. The oldest of these rules, originally formulated by Rayleigh, has been restated and clarified (76, 77) and requires that for any symmetry class all the frequencies remain constant or decrease mono-tonically with increase of mass. This places an upper limit on the frequencies of a deuterated species in relation to the hydrogen material. A second rule, of less strict validity, has been proposed (67) and gives a lower limit to the frequencies. The best known rule affecting two isotopically related molecules is the Redlich-Teller product rule (78). The rules connecting three or more isotopically related molecules are less well known, and of these the simplest is the sum rule (79), which relates the sum of the squares of the frequencies (i.e., the λ). A second order rule (80) relates the sum of the squares of λ, and of products of the λ. This type of rule has been generalized to higher orders in λ with special reference to the case of three isotopic species by Brodersen & Langseth (81) and was successfully applied to deuterated acetylene, ethylene (81), benzene (82), and other molecules (83). This work shows how, in favour-able cases, the frequencies of isotopic molecules can be calculated without knowledge of either force constants, or exact molecular geometry. This work also shows that, in these cases, the assignment of a third isotopic species provides no new knowledge of the force field and is therefore useless as a basis of choice between alternative force fields that fit the original isotopic species exactly.

These rules have been extended in an approximate fashion to cases where they do not apply in their exact form (81) and have also been shown to be approximately correct where replacement is made by a similar chemical species of atom rather than by an isotope (84), e.g., the calculation of OCS from CO_2 and CS_2 or of the mixed fluoro-chloroethylenes from $CF_2{=}CF_2$ and $CCl_2{=}CCl_2$.

Raman Intensities

In view of the considerable amount of interest in infrared intensities (1) it is relevant to examine the corresponding position for Raman spectra. This is less well developed mainly because liquids and photographic plates are used regularly in Raman spectroscopy. Photographic plates are notoriously difficult to use for accurate intensity work and the advent of photoelectric recording spectrometers (85, 86) allow more accurate measurements to be made.

Considerable difficulties remain associated with the use of convergent beams and polarizers, in order to obtain both a high intensity and a well defined geometry. Even so, the measurements are necessarily of relative intensity. The usual standard is the 458 cm.$^{-1}$ line of CCl$_4$ which is added to the liquid in known proportions; unfortunately, the proper correction for refractive index is not established with certainty since it is bound up with both cell geometry and effective volume (87), and also with internal field effects (88). Also, there is some doubt about the absolute value of the CCl$_4$ line intensity and the value that has been given (89) has been disputed (90). Fortunately, the development of direct intensity measurements on gases (91, 92) makes the work on liquids largely out-dated. In the gas phase the direct ratio of Raman/Rayleigh lines is measured directly and the absolute intensity of the Rayleigh line is simply related to the refractive index.

On the interpretational side, the main features parallel closely those of the theory of infrared intensities. The general theory has been discussed by Long (93) with particular reference to the Wolkenstein assumptions (94). These reduce the general problem by assuming that chemical bonds possess cylindrically symmetrical polarizability tensors and derivatives, which follow the bond direction when bending occurs. Such assumptions are unlikely to be correct for planar molecules, among others, but may not be seriously in error and have proven to be satisfactory for neopentane (95). It is also assumed that the polarizabilities and their derivatives are transferable between related molecules. Such a treatment has been only moderately successful for the series CCl$_4$, CHCl$_3$, CH$_2$Cl$_2$ (96), some group IV tetrahalides (97, 98), and substituted methanes (46, 99, 100), and is improved by terms that allow the mean polarizability of a bond to change with angle deformation. The benzene measurements (101) have been interpreted (102, 103) in terms of polarizabilities and their derivatives. The gas phase measurements on simple hydrocarbons (104) suggest that the rate of change of polarizability with C—H bond stretching is constant, and so the total C—H stretching intensities are proportional to the number of such links present.

The polarizability gradients in other gaseous hydrides (92), H$_2$, CH$_4$, NH$_3$, H$_2$S, HCl, and HBr, have been well correlated with the polarizability itself and with the values to be expected both at zero (combined atom) and infinite (isolated atoms) separations. The fact that polarizabilities are

monotonic functions of distance makes interpolations based on these more reliable than those based on dipole moments that probably have a maximum not too far from the equilibrium distance. This suggests that it may be possible for wave-function calculations to predict polarizability functions with better precision than those obtained from dipole moments (105).

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CHROMATOGRAPHY[1,2,3]

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Chromatography is, primarily, an analytical tool of extreme importance to industrial and academic research. Many thousands of published articles appear annually that show application to the petroleum, paint, drug, plastic, and many other industries. Anthony (1) reports that chromatography is used in approximately 50 per cent of the research reported in the *Journal of Biological Chemistry*, and this does not account for gas chromatography, which is rapidly expanding into the field. A new journal, the *Journal of Chromatography*, has been published to bring together the mushrooming interests in chromatography.

Interwoven in the vast literature of chromatography is a good deal of information of interest to physical chemistry. Besides providing a useful tool for analysis in reaction rate and other studies, chromatography is becoming very useful in obtaining experimental data on surface areas, sorption isotherms, and solution theory. In addition, the theory of chromatography is based primarily on physical-chemical concepts. The theories of adsorption, solution, nonequilibrium kinetics, and flow in porous media are among the important examples.

The material reviewed here places emphasis on the relationship of chromatography to physical-chemical concepts and methods. The two principal areas of interest are gas chromatography and paper chromatography. Ion exchange theory and chromatography have been reviewed in recent *Annual Review* papers, and will receive only brief mention here. Other types of column-liquid chromatography are treated briefly in the paper chromatography section. The general theory of chromatography will appear in the gas chromatography section since the greatest advance has been made here.

[1] The survey of literature pertaining to this review was concluded in December 1959. Gas chromatography includes pertinent references for a one-year period. Several review articles are cited for reference to previous literature. Paper chromatography has been reviewed for a two-year period.

[2] This work was supported by a research grant, A-2402 (C2), from the National Institute of Health, United States Public Health Service.

[3] The following abbreviations will be used: GAC, gas adsorption layer chromatography; GC, gas chromatography; GLC, gas-liquid chromatography; GSC, gas-solid chromatography.

GAS CHROMATOGRAPHY

Gas chromatography (GC) is of interest to the theoretician attempting to understand the chromatographic process because the comparative simplicity of a gas phase reduces the study to a consideration of the interaction of the migration solute with the immobile phase. He has one liquid solution (gas-liquid chromatography, GLC) rather than two, or a gas-solid interface (gas-solid chromatography, GSC) rather than a solid-liquid interface. Emmett (2) lists four applications of GC: (a) the analysis of vapors and gases, (b) the preparation of gram-size samples of pure compounds, (c) the study of adsorbents, gas adsorption, and the solubility and complexing properties of solutes with solvents, and (d) catalytic conversion studies with microcatalytic-chromatographic apparatus. To this we would add the promise of furnishing physical constants, e.g., boiling point, heat of vaporization, etc., formerly beyond reach either because of the instability of the compounds or the difficulty of obtaining sufficient quantities in pure form. Unfortunately, these goals are somewhat mitigated in GLC by the complexity of the immobile liquid phases commonly used. It is difficult to guess at interactions of the solute with this liquid when one uses high vacuum stop-cock grease, commercial detergents, and mixtures of isomers and polymers. Meaningful physical constants for such substances are generally lacking. "Polarity," as loosely used by the chromatographer, is essentially defined by chromatographic behavior itself and lacks quantitative definition. The use of bizarre partitioning agents stems from the use of GLC as a separations technique where expediency of separation is the key word.

We know of few areas where the literature is as well organized as it is in GC. In addition to general books (3 to 7), the communications presented at the London (8), Michigan (1957) (9), and Amsterdam (10) Symposia are available in bound form. At the time this review was written, the papers presented at the Michigan (1959) symposium were being collected for publication. The 1960 GC symposium was at Edinburgh, Scotland. Hardy & Pollard (11), Purnell (12), Trevino (13), Clough (14), Scott (15), Phillips (16), Rose (17), Ray (18), Magritte (19), and Hausdorff (20) have reviewed the subject.

The volume of literature and the interest in GC is so great that Lowry & Preston (21) have established an abstracting service. The abstracts are based on the original literature, printed on 5×8 in. punch cards, and distributed each week. They regularly survey some 150 journals, in several languages including Russian, and circulate first-hand reports of meetings in the United States and abroad. We consider this service a major contribution to the literature of this field and gratefully acknowledge their cooperation in preparing this review. This same group is ambitiously undertaking a similar service in instrumentation.

THEORY OF CHROMATOGRAPHY

Many reviews contain sections devoted to the theory of chromatography (11 to 14; 16, 17, 18, 22), which differ widely in approach and complexity.

Some writers make a distinction between GSC and GLC. Others divorce themselves from the physical nature of the phases involved and consider a general model without considering how it might be realized. Gerdes (23) considers repeated adsorption-desorption as the basis of separation. Hardy & Pollard (11), following the organization of van Deemter *et al.* (24), classify chromatography according to the type of distribution isotherm obeyed (linear or non-linear) and whether it is ideal (uniform flow of the mobile phase, uniformly packed columns, instantaneous attainment of equilibrium between the phases, and no longitudinal diffusion of the solute molecules). This gives four classes: (*a*) linear, ideal; (*b*) non-linear, ideal; (*c*) non-linear, non-ideal; and (*d*) linear, non-ideal. The last may be treated by stochastic theory, a material conservation approach, or the popular theoretical plate model (25). Giddings (26) points out that the last two are problems in non-equilibrium kinetics. Sen (27), using a stochastic approach, explains the movement and distribution of a solute on a GLC column by analogy to a Bernoulli trial system. Chmutov & Filatova (28) give a hydrodynamic model of a sorption column and illustrate the principal cases of the formation of chromatograms under different kinetic and hydrodynamic conditions. Bosanquet (29) considers only single fronts, which provide him with a means of investigating peak-spreading on migration. His formulae contain directly measurable constants, and he obtains good agreement between experiment and theory.

A great deal of information may be obtained from GC theory. If one is interested in separations then it is important to know which parameters affect the efficiency of the column, sharpness of the separations, and shape of the peak. As Hardy & Pollard (11) remark, efficiency may be divided into column efficiency as measured by the height of a theoretical plate and determined by the column design and operating conditions, and the solvent efficiency as measured by the ratios of the times two peak maxima take to travel through a column. The latter depends upon the ratio of the products of the activity coefficients and the vapor pressures of the pure solutes, which are determined by the column temperature and the nature of the solutes. These two measures are not completely independent, but it is very useful to make this separation. As factors affecting column efficiency, Hardy & Pollard (11) and Harris (22) list the carrier gas flow rate, nature of the carrier gas, pressure of the carrier gas, density of the column packing, particle size of the support, amount of solvent, length of the column, temperature, sample size, solute retention time, and conditions of sample introduction. No one of these measures has much meaning alone, since one may not always separate solutes on column with a large number of plates and, as opposed to this, one may have two peak maxima widely separated and yet have peaks so broad that they overlap. Martin *et al.* (30) suggest adopting a term, the column resolution, $2\Delta y/(y_a + y_b)$, where Δy is the distance between two peak maxima and y_a, y_b are the intercepts cut on the base line by the tangents to the two peaks. A similar expression has been suggested by Jones & Kieselbach (31). This seems to be a desirable measure. The broadening of

an elution peak is proportional to the square root of the number of theoretical plates, but the separation of elution peaks of different substances is proportional to the number of plates (22).

Flow in porous media.—The problems associated with fluid flow in porous media are of theoretical and practical interest in chromatography. First in importance is the dispersion, or zone spreading, caused by this flow. This effect is expected with all porous media, paper or column, but it has been studied especially in relation to GC under the name "eddy diffusion." Turbulence is not implied by this name, but rather the formal analogy with true eddy diffusion is meant. Dissatisfaction has been expressed with the name (32), and it is likely that something more appropriate may sometime be substituted.

In the introduction of the eddy diffusion concept into chromatography (24) it was asssumed that the term A in the van Deemter plate height equation

$$H = A + B/v + Cv \qquad\qquad 1.$$

was independent of velocity, v, and equal to several particle diameters. Many careful measurements, especially by Bohemen & Purnell (33) and Littlewood (34), have revealed A values that are very small or even negative. Considering the combined role of lateral diffusion and eddy diffusion, Giddings (35) has shown that eddy diffusion should be velocity dependent and has derived an approximate expression for this dependence. By this picture, eddy diffusion may well contribute practically nothing to plate height at ordinary velocities. The problem of a combined diffusion-flow pattern effect has also been treated by Saffman (36), but not in reference to chromatography. The difficulty of the problem is reflected in his results, which do not quantitatively reveal the general role of diffusion.

Several experimental methods have been used or proposed for the study of eddy diffusion. Glueckauf (37) has observed dispersion using a non-adsorbing medium, and has found no apparent velocity effect. A similar study has been made by Sen (27). These and other results have been summarized (35). Martin (38) has made the valuable suggestion that colored substances be observed as they run down a column. Jones (39) has observed that the eddy diffusion term is a function of the pressure and diffusivity of the carrier gas.

Barrer (40) has commented on another effect that has received insufficient attention: the influence of structure or tortuosity on the longitudinal diffusion term, B, in the van Deemter equation.

Golay (41) has studied systematic variations across the column diameter that increase plate height in large columns. An assumed variation within the packing and the increased flow in a space near the wall were investigated theoretically for their influence on plate height. Mixing washers were proposed as a remedy.

The analysis of flow in porous media is of particular importance in paper

chromatography where capillary forces act to establish concentration gradients in the mobile phase. This is discussed in the paper chromatography section.

Kinetics.—The term C in the van Deemter equation depends on the kinetics of mass transfer both between, and in, the stationary and mobile phases. As given by van Deemter *et al.* (24) for the penetration into a liquid film of uniform thickness,

$$C = \frac{8}{\pi^2} \frac{k}{(1+k)^2} \frac{d^2}{D}$$

2.

where k is the equilibrium ratio of the number of molecules in the stationary phase to the number in the mobile phase, and D is the diffusion coefficient of solute in the stationary phase. It is assumed in Equation 2 that diffusion through the liquid is rate controlling. This contention has been argued by Golay (32), who supports gas phase diffusion as the rate-controlling step in packed columns. In his theoretical treatment of coated capillary columns, terms are derived for both gas phase and liquid diffusion; the latter is rate controlling.

Expressions for the kinetic term in GC have also been derived by Young (42) and Beynon *et al.* (43). Young obtained the solute distribution by use of the Laplace transform. Resolution and retention time were discussed. Beynon *et al.* used a stochastic model to show the influence of rates in GC. Sen's (27) stochastic approach to rate effects has been mentioned.

Rate effects in ion exchange processes have received recent attention (44). Helfferich & Plesset (45) have made an important contribution by allowing, through the Nernst-Planck equations, for the influence of the diffusion potential on exchange rates. An interdiffusion coefficient D_{AB} was obtained, which is a function of relative concentration. The problem is thus non-linear, and computer calculations are required. Tien & Thodos (46) have also examined a non-linear ion exchange problem; in this case the equilibrium at the bead interface is of the Freundlich type. The diffusion rates were assumed to remain constant, however. The problem of non-linear rates or non-linear equilibrium with rate effects included is still one of the difficult and important problems that needs much more investigation.

The expression for C (Eq. 2) is clearly a simplification for packed columns since a uniform film cannot possibly be present. Baker *et al.* (47) indicate the accumulation of stationary phase in pores of varying size. Purnell (48) discusses the increase in C (as well as A) due to the mixing of mesh sizes. He also finds C to be proportional to mesh size.

Habgood & Hanlan (49) have attempted to evaluate rate factors using steam-activated charcoal as the stationary adsorbent. Equation 1 was used. There appeared to be a greater resistance to mass transfer for samples of least activation. Janak (50) has discussed the role of centers having different adsorption energies. Such heterogeneous adsorption processes have been treated theoretically by Giddings (51, 52). By assuming the various kinetic

processes to be occurring near equilibrium, an equation is derived that shows the spreading of peaks due to kinetic processes of arbitrary complexity. The presence of adsorption sites of n different kinds has been evaluated, along with the role of consecutive reactions, the sorption of large molecules, and the occurrence of chemical reaction. The method has been extended to diffusion-controlled processes in evaluating the effect of coiling and bending on column performance (53).

Plate height and zone profile.—It is an ideal situation if solute can be injected as a delta-function at the column inlet. Most of the calculations in which experimental data are compared to theoretical equations are based on this assumption. To make the comparison valid, plate height should be extrapolated to zero solute load (33). Furthermore, the plate height increase due to the detector and injection system must be subtracted out (54). Under these ideal experimental conditions, a solute peak emerges nearly as a Gaussian profile. The column plate height is obtained as $H = LW^2/16t^2$, where L is the column length, W the width of the peak (four standard deviations), and t the solute retention time in the same units as W.

Numerous experimental parameters determine the plate height. Purnell (48) has shown the influence of particle size and uniformity, amount of stationary liquid, and the nature of the carrier gas on A, B, and C of Equation 1. The eddy diffusion anomaly was discussed. The effect of non-linearity in the initial part of the column was related to allowable solute load. Here, as in Bohemen & Purnell (33), the plate height was found to decrease with smaller solute loads throughout the experimental range. This contradicts the conclusions of Bethea & Smutz (55) and Bethea & Wheelock (56), who found a minimum plate height at non-zero solute load. No theoretical justification was given for the latter conclusion.

Various factors affecting plate height have also been discussed by Harris (22), Littlewood (34), and deWet & Pretorius (57). Littlewood used glass beads for the solid support. He showed, theoretically, that the volume of the introducer contributes both to A and B of Equation 1. The temperature dependence of C was also studied. The effect of the carrier gas on plate height was discussed by Vyakhirev & Bruk (58). Cornish (59) has compared theoretical and experimental plate height expressions in relation to ion exchange chromatography. Golay (32) derived rigorous plate height expressions for capillary columns.

The influence of pressure gradients within a GC column has been studied by Stewart, Seager & Giddings (60). They conclude that the plate height, when measured as described above, differs from the local plate height in the column. Correction factors are deduced for comparing the two. Littlewood (34) derived a similar corrected equation by calculating average column properties. Villalobos, Brace & Johns (61) have derived an equation for separation with backflushing, an effect due to the pressure gradients.

Emerging chromatographic zones are never strictly Gaussian in profile. Major deviations from Gaussian can be caused especially by non-linear

equilibrium (next section), by injection of solute not as a delta-function (frontal analysis is an example), and by the effects of the detection and injection devices. Johnson & Stross (54) found the shape, width, and position of the peak maxima to depend on katharometer design. This paper should be carefully considered by those interpreting GC data based on katharometer detectors.

The diffusion at a front (frontal analysis) has been studied by Bosanquet (29). Allowance has been made for the variation in gas flow velocity due to loss and gain of solute by adsorption and desorption. The difference between the spreading of advancing and receding fronts can be very large. This effect has been used (62) to explain observations regarding the relation between peak height and concentration. Fejes & Schay (63) outline the possibility for steady fronts when diffusion can be neglected.

Glueckauf (64) has derived equations for the position and shape of zones of highly radioactive gases where the local generation of heat is important chromatographically.

Said (65) has used tables and charts of the Poisson distribution for obtaining the concentration profiles of columns with less than 200 plates. He (66) also deals with the difference between experimental and true elution curves using finite sample size and dead free volume at the bottom of the column, and has studied nonhomogeneous columns (67).

Thermodynamics.—GSC often involves non-linear adsorption isotherms. Gregg & Stock (68) have shown that concentration profiles can be calculated in practice from a detailed knowledge of the isotherm and vice versa. They have examined the five types of Brunauer-Emmett-Teller (BET) isotherms and have verified their conclusions experimentally. Adsorbed water can change the type of isotherm. Fatt & Selim (69) have recently demonstrated mathematically that "stepped" concentration profiles are obtained with solutes having a maximum in their adsorption isotherms. Hanlan & Freeman (70) gave a comprehensive treatment of GSC based on the equation of Halsey *et al.* for the interaction of gases and solids. The retention volume of the former was identified with the apparent volume of the latter, linking static measurements to GC. Wolf & Beyer (71), applying the theories developed for GSC, used the method to determine relative surface dimensions of adsorbents and to obtain data on their pore systems and adsorptive strengths. Results were compared with those obtained by BET adsorption isotherm methods. Roth & Ellwood (72) and Cremer (73) have used GSC to determine the surface areas of powdered catalysts. The results were in good agreement with those obtained by conventional volumetric methods in a vacuum system. The decrease in catalyst surface due to poisoning can be determined rapidly and easily by GC.

White & Cowan (74), arguing from thermodynamics, have examined the factors that give rise to symmetrical elution curves and retention times that are independent of sample size in GLC and have related the partition coefficient to the concentration and to the heat and entropy of solution. Wolf

& Ternow (75) used four silica gels that differed in surface and pore distribution and size as solid supports for varying amounts of liquids. Partition coefficients of hydrocarbons decreased as the proportion of immobile phase to support increased. With 15 per cent liquid, partition coefficients varied with the structure of the gel. This variation was discussed with regard to the combined effects of the gel structure and polarity of the immobile phase.

Cremer (76) defines gas adsorption layer chromatography (GAC), intermediate between GSC and GLC, as a special case of GC in which partition occurs in a layer of material adsorbed on the solid support. If the layer is monomolecular, the process is termed "mixed adsorption"; if multilayered, the process is called "solution" and becomes GLC. Most untreated adsorbents have such an adsorbed layer, which becomes a liquid only when its vapor pressure remains constant on increasing the amount of condensed material. Up to this point, use of the adsorbed layer is GAC. A desirable effect that results is the blocking of very active adsorption sites in a heterogeneous surface; producing a homogeneous surface and reducing tailing since the retention is by weaker sites, e.g., squalane as a tailing reducer. Symmetrical elution curves and a faster breakthrough are produced. A quantitative treatment of GAC is given in which retention time of a substance is related to the temperature, adsorption enthalpies, and surface areas. Particular cases are considered and experimental results are discussed in relation to theory. Schultze & Schmidt-Küster (77) investigated the resolving power of three silica gels of differing porosity and the effect of impregnation with dibutylphthalate. The effect was most marked for fine-pored gel and the initial amount of liquid. The resolution as affected by various carriers was also demonstrated. Brodský & Zmítko (78) report their results with silica supporting dioctyladipate. Scott (79) studied alumina of varying activity. Alumina covered with a monomolecular layer of water gave the best results. Certain pairs, not resolved on this material, were separated if 2 per cent silicone oil was added to the alumina before deactivating it with water. Janak, Krejci & Dubsky (80) report on Linde 5A molecular sieve and the change in adsorbent properties with a progressive release of water.

Activity coefficients, and heats and entropies of solution may also be determined from GLC data (11). Kwantes & Rijnders (81) demonstrated the relationship between partition coefficients and activity coefficients, and calculated activity coefficients for non-polar and polar solutes in both non-polar and polar solvents. Results were compared with activity coefficients determined by other means. For polar solutes on non-polar solvents, lack of agreement was attributed to residual adsorption of the supporting material. Agreement was obtained when metal helices were used as the solid support. Hardy (82) has determined activity coefficients at infinite dilution for a series of compounds on several stationary liquids in the 20–100°C. range. Pyke & Swinbourne (83) have used GLC to determine heats of solution. Jentzsch & Bergmann (84) determined retention ratios at different tem-

peratures and compared these with corresponding vapor pressure ratios calulated from thermodynamic data. Agreement between vapor pressure ratios and empirical ratios was generally good. Deviations were attributed to a variation of the activity coefficient from unity.

For isomers and homologous series, retention ratios may be calculated with reasonable accuracy from vapor pressure ratios if solute interaction with the stationary phase is equivalent to the intermolecular influence between pure compounds in the condensed state. Immobile phases showing this type of behavior may be referred to as boiling point separators since the emergence is ordered according to boiling points. This could be useful to the physical chemist in determining vapor pressures and heats of vaporization of either very small samples or of compounds that decompose before reaching their boiling point. In the latter case one need only run a chromatogram below the decomposition temperature. Of course, one must be satisfied that his immobile phase is indeed a boiling point separator with respect to the compound under consideration. The technique seems a likely alternative to determination of vapor pressures from vacuum distillation procedures. This type of behavior is also very useful in classifying immobile phases with regard to the mechanism of retention. Takamiya, Kojima & Murai (85) derived an equation relating retention volume to solubility parameters of gas and stationary liquid. Warren, Warren & Yarborough (86) have correlated GC separations with extractive distillation separations by comparing GC partition coefficients with relative volatilities from equilibrium still data. Bayer & Röck (87) define a selectivity coefficient, which is the ratio of retention volumes with respect to a single standard for two substances that have the same boiling point but belong to different homologous series. The selectivity coefficient becomes the ratio of activity coefficients in this case. Thus we have passed from a consideration of compounds of the same homologous series with different boiling points to compounds of different series with the same boiling point.

Jentzsch & Bergmann (88) used the retention ratio to characterize the selectivity of stationary phases. They also discuss resolution in relation to zone shape. As a measure of overlapping for zones of the same height, they use the height of the point of intersection expressed as a fraction of the maximum height. Preston (89) has derived a relationship between partition coefficients calculated from retention volumes and vapor equilibrium constants (K-values) that involves the molecular weights of the carrier gas and stationary phase and the density of the carrier. The results are in agreement with partition coefficients determined by other methods. The variation of K-values with the molecular weight of the immobile phase is thought to parallel the variation of K with convergence pressure. Mellado (90) has determined partition coefficients for methane through butane on n-dodecane and calculated K-values. Agreement with the NGAA (Natural Gasoline Association of America) correlation of K-values is excellent for butane but

decreases with the decreasing molecular size of the solutes. He uses partition coefficients to calculate heats of solution, excess of free energy and entropy of solution, relative volatilities, and van Laar constants.

Column packing and partitioning agents. Solute-solvent interaction.—It is a dangerous oversimplification to assume that the solid support does not participate in the partitioning process in GLC and that retention is solely by solution in the liquid. The nature of the support has little effect on the separation when the solutes show little adsorptivity (hydrocarbons, esters, ethers), but there is a marked effect for adsorptive solutes (amines, lower alcohols, acids). Liquid paraffin or silicone oil immobile phases frequently show tailing. This is eliminated with dioctylpthalate (DOP), tricresyl phosphate (TCP), or glycerine (91). Assuming that the immobile phase completely wets the adsorbent to give a multimolecular layer, then solute adsorption must be from the liquid solution. It is plausible that DOP and TCP reduce the activity of these adsorption sites by their own adsorption while the paraffins do not. Ottenstein (92) remarks that diatomaceous earth materials have both acidic and basic sites that interact with appropriate functional groups of the solutes to produce adsorption and subsequent asymmetry. He reviews methods of either removing these sites or covering them. Omerod & Scott (93) coat their support with gold or silver before loading it with immobile liquid. Silver almost eliminated peak asymmetry. Desty, Godfrey & Harbourn (94) compared Celite 545 and C22 firebrick as a support for a paraffinic wax. Effects of particle size, flow rate, and retention volume were considered in relation to the van Deemter equation. Baker, Lee & Wall (47) have studied the effects of surface area, pore volume, pore size distribution, and particle size on GLC columns. They conclude that most of the liquid is located in the finest available pores with a thin layer over the remaining surface. Plate height showed a minimum with a certain concentration of liquid depending upon the fine pore structure. This raises the question of the effect of diffusion of solute molecules into and out of the liquid in very tortuous small pores as contrasted to the process in shallow surface puddles. These authors outlined the properties of a desirable support. Decora & Dinneen (95) obtained symmetrical peaks with basic nitrogen compounds on non-polar liquids supported by Tide (Proctor and Gamble) pretreated with potassium hydroxide. Horning, Moscatelli & Sweeley (96) apply a silicone coating to pretreated Celite before it is used as a support for a polyester immobile liquid.

Johnston (97) and Bayer (98) list some generally useful partitioning agents and some general principles for the selection of stationary phases. Tailing of polar compounds when using a firebrick support may be prevented by additives to the liquid phase. Kieselguhr is a satisfactory support in all separations.

Rohrschneider (99) graphs the logarithm of the retention ratio of n-butane and 1,3-butadiene vs. solvents arranged according to their "polarity" to obtain a slightly curving plot. He discusses the influence of "polarity"

on liquid-gas intermolecular forces and gives a graphic determination of a suitable ratio of lengths for coupled columns with phases of different polarity. Rijnders (100) reported on separation of hydrocarbons on several liquids, including saturated silver nitrate-benzyl cyanide and active adsorbents holding liquids. Langer, Zahn & Vial (101) studied the synthesis, and the physical and complexing properties of alkyl tetrachlorophthalates which hold promise of utility in the separation of aromatics. The separation seems to depend on the electron donor characteristics of the aromatics. Karchmer (102) resolved a mixture of sulfur compounds boiling over the range 58–126°C. on beta,beta'-iminodipropionitrile, which separated the solutes according to their electrophilic character. This was then coupled with a white oil column, which separated solutes according to their volatility. A log-log plot of retention volumes on these two liquids gave a series of straight lines corresponding to particular structural features of the solutes. Fitzgerald (103) concluded, from an extensive investigation, that non-polar liquids retain ortho-alkyl substituted phenols, but polar phases release them earlier than unsubstituted phenols of equal volatility. Janak, Komers & Sima (104) and Janak & Komers (105) discuss selectivity for monohydric phenols as it is influenced by the number of hydroxyl groups in the stationary phase, by polarity, and by the formation of hydrogen bridges. Janak & Komers (106) extended the investigation to dihydric phenols.

DuPuy & Story (107) suggest GLC as a means of detecting intramolecular hydrogen bonds between OH-groups and carbon-carbon double bonds. James (108) differentiates between the behavior of saturated and unsaturated esters on polar and non-polar phases: the unsaturated moving faster than the saturated on non-polar phases and slower on polar phases. On non-polar phases, zone position depends upon both number and position of double bonds; on polar phases, position does not alter behavior. James (109) also discusses the use of two chemically different immobile phases to determine chain length, position of double bonds, and configuration about these bonds. The argument is supported by data for 40 C_8–C_{22} fatty acids. Lipsky, Landowne & Godet (110) and Lipsky & Landowne (111) also discuss the effects of the chemical composition of the immobile phase on retention of acid esters. Hawke, Hansen & Shorland (112) use retention volume plots on different phases to identify esters. Dimick & Chu (113) investigated efficiencies and separation factors for the GLC of fatty acid methyl esters on polyesters of molecular weights up to several thousand. This exploitation of structural features is also exemplified by Shabtai, Herling & Gel-Av (114) in their separation of the isomers of the methylcyclopentenes and methylcylopentane, and ethylcyclopentenes and ethylidenecyclopentane, on silver nitrate in glycol. Some isomers differed by as little as 0.1°C. in boiling point. The use of liquids that contain silver nitrate to separate unsaturated and saturated compounds is quite common.

Beaven, James & Johnson (115) found that differences in the ultraviolet spectra of ortho-substituted biphenyls closely paralleled correspondingly

large differences in retention volumes. The alteration in spectra that accompanies steric interference with planarity, and hence resonance, is well known. That this effect should also appear in GC behavior is very interesting. Kelker (116) tabulates the effective retention volumes of 77 compounds on two liquids and suggests a graphical representation useful in identifying unknowns from relative retention volumes. Young (117) has made a careful study of the linear variation of the logarithm of the retention volume with respect to several parameters and while discussing the results with regard to structure introduces the concept of a "family plot." Kovats and co-workers (118 to 120) define a "retention index" which, for non-polar phases, is simply related to the solute boiling point. The parameter shows only a small, linear dependence on temperature and is independent of column constants and the type of apparatus used. It holds promise of characterizing organic compounds and elucidating structures of unknown solutes as demonstrated by its application to aliphatic, cyclic, and aromatic compounds. Barber *et al.* (121) investigated retention times relative to mesitylene of homologous series of organic compounds chromatographed on molten heavy metal stearates and compared the results to those obtained on Apiezon L grease. Particularly strong interactions were found with amines.

The above references demonstrate advances in the understanding of the fine interplay of forces as determined by the structure of solute and partitioning phase, and the use of such hard-won knowledge in structural determination of unknown solutes. This has long been a goal of chromatography. This is a very fertile field of investigation, and it is encouraging to see advances in this direction.

High temperature and temperature programmed GC.—The finding of satisfactory immobile liquids is a problem at high temperatures. Alexander & Marsh (122) report maximum operating temperatures for several liquids, including fused salts. The separation of biphenyl and isomeric terphenyls at 445°C. by Baxter & Keen (123) demonstrates high temperature accomplishments of GLC.

Samples of solutes covering a wide boiling range offer special problems. At low temperatures, where the low boiling liquids have reasonable retention times, the high boiling components take too much time and show serious peak spreading. At high temperatures, the low boiling liquids come through too fast and are not resolved. A solution to this is to increase the operating temperature uniformly and in a known manner during an analysis (temperature programming). Wiersma & Tollefson (124) have related their experience with the technique. Dal Nogare & Harden (125) described an apparatus for heating rates of 2.5–30°C. per minute. Because of the change in flowrate with temperature it is equipped with a constant flow controller. Under these conditions the pressure drop across the column must change, an effect that complicates the theoretical treatment. Temperature-programmed and isothermal analyses of paraffin mixtures are compared. Martin, Bennett & Martinez (126) and Habgood (127) have attempted the predic-

tion of retention times in a temperature-programmed analysis from iso-thermal data. Clough (128) emphasized that all factors other than tempera-ture must be rigidly maintained as constants in temperature programming. Peak areas must be used as the criteria of concentration.

Reporting GC data.—Rijnders (129) feels that one per cent is a reasonable standard accuracy in GC retention data. Retention volumes should be measured as the product of retention times and flow rates as accurately de-termined by a stopwatch. The retention volume of a permanent gas which, in practice, is generally air, is usually subtracted to give the reduced reten-tion volume. Relative retention volumes are the ratio of these values and ought to be determined in the same run. Retention volumes should not be reduced to 0°C. since they are only significant at one temperature. Retention volumes should be determined using non-participating supports, and sample sizes should be small enough to avoid non-linear isotherms, finite evapora-tion times in the sample injector, viscosity changes, etc. Oster (130) sep-arates factors affecting accuracy into those due to the column and those due to auxiliary apparatus. He remarks that one can ascertain up to what point velocity peak broadening is caused by axial molecular diffusion by using a plot of peak height for an inert gas vs. carrier flow rate. A French committee (131) suggested a standard system of notation for expressing re-tention data and proposed it for international adoption. Ambrose, Keule-mans & Purnell (132) and Johnson & Stross (133) have made similar sug-gestions. Scholly & Brenner (134) reported retention data for 18 different mixtures representing a wide variety of chemical types on nine popular sta-tionary liquids. Ambrose & Purnell (135) reduced published retention data, including temperature effects, to the form recommended by the Committee of the Gas Chromatography Discussion Group (132). Empirical constants for the temperature variation of retention volume were given. The *Journal of Chromatography* has been collecting and reproducing already published GC data. This, along with the abstracting service, constitutes a valuable contribution to the field.

Applications.—The applications of GC are legion. We can but briefly indicate those of possible interest to the physical chemist. Brenner (136) has discussed the advantages and limitations of GC as a microanalytical tool. Guild & Bingham (137) summarized techniques that permit the analysis of mixtures of components differing widely in properties. Harbourn (138) has reviewed well-established methods of quantitative use.

A great deal of interest has been created by adapting sample injection units to hold a tube containing catalysts over which a reactant may be passed as a "plug" or continuously, and then directly into the column for analysis. One such device has been described by Ettre & Brenner (139). It has been used in the analysis of products that resulted from passing isobutyl-ene over a silica-alumina catalyst at 600°C. Hall, MacIver & Wever (140) used it in catalytic cracking and polymerization studies; Keulemans & Voge (141) with napthenes over a platinum reforming catalyst; Pitkethly

& Goble (142) in the measurement of adsorption-desorption processes and reaction kinetics over heterogeneous catalysts at very low surface coverage; and Ridgway & Schoen (143) in a study of hexane isomer equilibria over various catalysts.

Knox (144) points out the advantages of GC in kinetic studies. The fact that nine of the papers presented at the *Symposium on Isomerization and Related Processes* at the 135th Meeting of the American Chemical Society involved the routine analytical use of GC indicates the value of this tool in elucidating kinetics and mechanisms.

PAPER CHROMATOGRAPHY

While many papers are written annually on the separation and identification of compounds by paper chromatography, very little notice is taken of the physical chemical aspects. The multitude of unknown variables in any single procedure limits information as to the molecular processes involved. Paper chromatography differs uniquely from other chromatographic procedures by virtue of the capillary flow mechanism and the role played by the cellulosic (usually) nature of the stationary phase. Space allows only brief mention of books (145, 146) and review material that are concerned with separation and detection techniques.

THEORY OF PAPER CHROMATOGRAPHY

The more general aspects of the theory of chromatography have been discussed above and only those problems unique to the use of paper as the stationary phase need be discussed here.

One such problem is the movement, in part, of the mobile phase (developer) through the stationary phase by capillary forces. This establishes a concentration gradient of developer in the stationary phase. Gillespie (147) has derived approximate expressions for the capillary rise of a liquid against the forces of gravity. He assumes a uniform concentration in the initial part of the strip, and a permeability varying with the third power of concentration. Capillary penetration into paper has also been studied by Nakagaki & Osagawa using a pore model (148). A more detailed analysis has been presented by Ruoff *et al.* (149) in which the flow has been analyzed by the mathematics of diffusion. Flow in a particular paper-solvent system is characterized by a concentration (of developer in paper) dependent diffusion coefficient. This allows the prediction at any time of the concentration profile in the paper for both linear and radial flow. The effect of external force fields has not yet been treated. This work serves as a basis for the study of the effect of solvent concentration gradients on zone migration. The latter shows the dependence of the R_f on initial zone location and time of development (150). R_f (linear) and R_r (radial) are derived, and the relationship $R_f = R_r^2$ is discussed.

The influence of concentration gradients and external fields is magnified in the newly developed technique of centrifugal chromatography (151, 152).

No theoretical treatment of flow rates or R_f has yet been presented for this method. High temperatures have also been utilized to increase flow rates (153, 154). The influence of paper geometry on flow rates has been calculated by Ruoff & Giddings (155). The results are qualitatively confirmed by Furuhawa (156).

Thermodynamics.—The usual thermodynamic consideration of R_f values is based on the Consden *et al.* (157) formulation of the partition coefficient in which developer concentration gradients are neglected. The partition coefficient depends on the chemical potential difference of the solute in the two phases. Each structural unit may be considered as contributing an additive fraction to the total chemical potential of the solute in each phase. Dikstein (158) has presented a theoretical basis for Martin's (159) postulated contribution of a chemical potential for groups and has shown how an approximate value can be calculated from molar volume and the solubility parameter. Neglect of solvent-cellulose interaction and gradient effects are partially responsible for discrepancies between experimental and calculated R_f's. Moore & Baker (160) have used similar considerations, including a factor for bond contributions, to predict R_f values for 88 synthetic peptides in 15 solvent systems. The calculated R_f's agreed with experimental values to within ± 0.05. In a study of the correlation between structure and R_f in the paper chromatography of flavonoid compounds and tannins, Roux & Evelyn (161) demonstrated a linear relation between R_m of these compounds, i.e., $\log(1/R_f - 1)$, and the number of substituted hydroxyl groups. Exceptions to this linear relation could be attributed to intramolecular H-bonding of the hydroxyl groups. This and earlier work on the flavonoid pigments has been reviewed by Harborne (162). Lederer (163) has used similar considerations to correlate the R_f of Pa(V) ion with solvent composition showing that R_m is linear with the p_{Cl^-}. The relation for a homologous series of dicarboxylic acids has been given by Sanda *et al.* (164). Franc & Jokl propose that the chemical potential contribution of homologous units in side chains of molecules is a logarithmic rather than a linear function (165). A general discussion of the problem of "group constants" for the calculation of R_f is given by Decker (166). He has further proposed (167) the use of $R_{circular}$ as a means of eliminating the gradient effects inherent in R_f, thus providing a more reproducible value. However, the use of the method discussed above (150) does provide a partition coefficient independent of gradient effects.

A series of papers by Kertes (168) suggests the use of chromatography as a rapid method for surveying solvent systems for extraction processes for inorganic ions. The R_f value and related partition coefficients for 58 ions in several systems have been reported. Unfortunately, no consideration of adsorption of ions has been included, and no proof of similarity between the calculated chromatographic partition coefficients and extraction procedures can be assumed. A further complication is the evidence that the presence of ions (169) and solutes (170) lead to deviations from independent migration of spots. When the partition coefficient is a function of the pH of

the developer, this may be included in the R_f formulation as proposed by Waksmundzki & Soczewinski (171), who suggested this as a basis for surveying buffer systems for counter-current distribution. The work of Hordis & Kowkabany (172) in radioactive studies of materials deposited along the chromatographed spot path in supposed pure partition chromatography of sugars shows that the differentiation between partition and adsorption methods is one of degree and not of kind. Further evidence is found in the literature on artifacts noted below.

Stationary phase, developers, and solutes.—The role of the stationary phase in partition chromatography has not been the subject of extensive study. The importance of a better knowledge of its properties has been pointed out by Stewart & Shin (173) in their consideration of its composition and structure. They point out that molecules larger than 40 A diameter will meet large resistance to diffusion through the stationary phase within the cellulose fiber. Evidence of this is seen in the study of the R_f of steroids in impregnated paper where R_f increases to a maximum with an increasing stationary phase (174). The swelling of cellulose in various solvents has been discussed from a thermodynamic viewpoint by Thode & Guide (175) who apply the Hildebrand solubility parameter concept. Jakubec (176), using water for both phases, has shown an increase in the partition coefficient with an increasing saturation of the stationary phase. The variable partition coefficient indicates a change in the chemistry of the stationary phase. The polarity of the stationary phase appears to be its only property that has received general acceptance as an important variable. On this consideration, numerous special stationary phases have been proposed, for example, natural rubber (177), silicic acid (178), formamide (179), acetylated paper (180), cellulose phosphate paper (181), ion exchange resins (182, 183), and glass paper (184). Obviously, some of these impart exchange and adsorption properties to the stationary phase.

The need to equilibrate the stationary phase with the moving phase to prevent chromatographing of the solvent and anomalous spot shapes was illustrated by Coch-Frugoni (185). The simplicity of operation (186) and high resolution (187, 188) recommends the use of circular chromatography when only a small number of components are to be separated.

Little theoretical progress has been made in the selection of developers. For organic systems, the use of formamide and related compounds has been found to increase the polarity of the moving phase (189). Use of salt concentration gradients (190) or developer changes (191) essentially increases the number of experimental parameters in the chromatographic method but, so far, selection of the solvent system is an art (192, 193). Adding indicators to the solvent (194, 195) to mark the front of the solvent band does not appear to have any appreciable effect on R_f. If the material being chromatographed is not readily mobilized, as is particularly true in the case of metal ions, recourse can be made to complexing agents (196). In like manner, to overcome interactions with paper by molecules having active functional

groups, it has become common practice to form derivatives such as esters of organic acids and phenylosazones of aldoses (197). The reader is referred to the analytical literature. These derivatives are often somewhat labile and their dissociation leads to tailing, double spotting, and other artifacts (198). Long trails known as "comets" and also multispotting as the result of ionization have been reviewed by Zweig (199), who observes that caution must be taken in interpreting unknown chromatographic spots. The distribution of solute and spot shapes have been derived theoretically for multispotting caused by slow reaction rates [Keller & Giddings (200)]. The attempts to quantitate chromatograms by measurement of spot size has been reviewed by Giddings & Keller (201) and the derived equations are related to data in the literature. They derive the relationships that spot-area is directly proportional to log spot-content and spot-length is directly proportional to the square root of log spot-content. Kauman & Bak (202) have discussed the shape of a spot as a function of sorption rates in paper chromatography. Weber (203) has analyzed the basic differential equations for zone shape in an attempt to explain "comet" shapes in discontinuous electrochromatograms. He shows that in a continuous electrochromatographic process in which buffer solutions stream through the support at right angles and where the separating mixture enters at a constant point, adsorption does not have any troublesome influence. The importance of the pH of developers for ionizing solutes is shown by Betina (204), who illustrates transition of spot shape with changes in ionic species as a function of pH. Use has been made of complexing agents in the solvent (205) to remove interfering ions to prevent tailing and other artifacts (206). However, interaction between solute and solvent can also lead to artifacts (206).

A large number of separations have been implemented by recent developments in column-liquid chromatography. The book by Lederer & Lederer (207) remains the most comprehensive source of material on this subject. A review of adsorption and precipitation chromatography has been presented by Hayek (208). The principal physical-chemical interest lies in a few of the theoretical results described in the GC section on theory. Important developments in the field, differing from the concepts reviewed above, include the separation of molten salts on glass powder columns (209) and the correlations of isomeric separations with stereo-configuration (210).

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NUCLEAR AND ELECTRON RESONANCE

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Introduction

This review is intended to be a survey of progress in spin resonance as published between December 1, 1958 and December 1, 1959. For want of space, it has been generally necessary to exclude references to work published earlier. Reports on experiments in chemistry, sometimes important ones that relied on resonance mainly for analytical purposes, have also, regretfully, been omitted. Significant omissions have been made in the fields of electron and nuclear resonance in antiferromagnetics, in double resonance, in experimental technique generally, and in motional narrowing of proton resonance lines. The last-mentioned short-coming may be relieved by the fact that the set of papers given at a conference in London on this subject, April 1959, have been published in the *Archives des Sciences de Geneve*, Volume 12, fascicule spécial pp. 1–245.

Nuclear Quadrupole Resonance and Couplings

An isotopic fine structure on the quadrupole resonance line has been found in BCl_3 (1, 2), BBr_3 (2), BI_3 (3), and Cl_2 (4, 5). In the boron halides, the effect comes from the fact that a halogen atom bound to a B^{11} atom sees a different effective field gradient than the halogen bound to a B^{10} atom. The quadrupole resonance frequencies in a solid are proportional to a mean electric field gradient, the average being taken over the intramolecular vibrational and the torsional intermolecular vibrations. Fine structure should be observable in isotopically enriched compounds in which C^{12}—Cl bonds are present.

The dependence of the quadrupole resonance frequency on torsional vibration averaging leads to a temperature dependence of the quadrupole resonance frequency that can become sharp when there is an abrupt change of the state of motion in the crystal. In CH_2Cl—CH_2Cl, for example, a second order phase transition, a narrowing of the proton resonance, and a rapid broadening and eventual disappearance of the Cl^{35} signal all occur in the same temperature range (6).

In 1,2-dibromoethane (8), as in $Li_2SO_4 \cdot D_2O$ (9), the resonance is seen at low temperatures, then becomes broadened to invisibility and at a higher temperature is seen again. In the intermediate range, the correlation time for reorientation is comparable with the reciprocal of the resonance frequency. In 1,2,3-trichlorobenzene (7), on the other hand, the proton line width remained steady while the quadrupole lines broadened with increasing temperature. The crystal disorder here increases without any comparable increase in amplitude of molecular motion.

The main application of quadrupole resonance is in the determination

(with some assumptions) of the molecular charge distribution. For substituted chlorobenzenes, the equation $f(Cl^{35}) = 34.826 + 1.024 \, \Sigma \sigma_i$ (10), where f is the Cl^{35} resonance frequency in Mc./sec. and σ_i is the Hammett substituent parameter, has been shown to agree closely with experimental data. Chlorosubstituted heterocyclics have recently (11, 12, 13), been examined and it is found that when nitrogen is in the ring, as in pyridine and pyrimidine, the frequencies are not very different from those predicted by the above equation. Yet, the asymmetry parameter for Cl has been found to be 0.24 in cyanuric chloride (14, 15), in contrast to 0.08 in paradichlorobenzene. Evidently, the polarity of the ring nitrogen atoms that tends to draw charge from the ring, making the C—Cl bond less ionic and raising the frequency, is compensated by the increased double bonding of the Cl atoms, which tends to lower the resonance frequency. The increased double bonding actually follows from a theoretical (15) study of the ring π state energy levels. In thiophene the frequencies tend to be higher than the equation would predict, suggesting that the sulphur atom is attracting electrons from the ring.

Quadrupole resonance supplies a rather complete description of the molecular wave function in compounds in which the resonances of several types of nuclei have been observed, as in the alkali chloroiodides (16, 17) such as Cs ICl_2, and in the Group III halides (18) such as Al_2Br_6 and In_2I_6. In both these cases, halogen atoms are multiply bonded; the use of multi-center (i.e., delocalized) bonds made it unnecessary to introduce d-hybridization of the halogen atoms to explain the results. In bridge structures as occur in Al_2Br_6 the bridge halogens have less negative charge than the terminal ones and the bridge bonds are probably bent.

N^{14} resonances have been observed in zero field in symmetrical tertiary amines (19), alkyl and halocyanides (20), and in N_2 (21), compounds in which the asymmetry parameter, η, is zero or nearly so. It was pointed out (22) that to detect a resonance in which the N^{14} nucleus had a large asymmetry parameter, the amplitude of modulation would have to be exceedingly large. Recently (23, 24), N^{14} resonances have been seen in p-Br aniline, p-Cl aniline, p-amino aniline, and urea with the use of 50 gauss modulation. The eq Q's (Mc./sec.) and η were respectively 4.135, 4.117, 3.910, 3.507 and 0.231, 0.243, 0.264, 0.323. Most of the decrease in quadrupole coupling constant in this series is accounted for by the increase in asymmetry parameter. The latter arises from a σ effect (in that the nitrogen atom is bonded to two hydrogen atoms and an sp^2 hybridized carbon atom, which is more electronegative than the hydrogen atoms), and a π effect (whereby the nitrogen atom loses π electrons to the conjugated system).

Using the best available (25) wave function for NH_3, the electric field gradient at the N nucleus has been calculated (26). Combining this result with the experimental eq Q^{14} in gaseous NH_3, a value of 1.08×10^{-26} cm.^{2} is obtained for Q^{14}, the quadrupole moment of N^{14}. The answer is reasonable, yet the same wave function would give a very bad value (27) of the quadrupole moment of the deuteron so that the wave function is clearly wrong at some parts of the molecule.

Quadrupole coupling constants involving the B^{11} nucleus have been studied by observing their effect on the magnetic resonance. In general, a boron atom that is four or six coordinated has a small coupling constant but if it is bonded to two or three atoms it has a large coupling constant. An example is boron carbide $B_{12}C_3$ (28) with icosahedra of B atoms, each of which is bonded to five other B atoms in the same icosahedron plus a sixth atom that is either a B atom in a neighboring icosohedron or a C—C—C chain. These B atoms have small field gradients, but examination shows that there is a small resonance with a large field gradient that results from B atoms replacing the central C atoms of the C_3 chain as a substitutional impurity. Boron glasses of composition $B_2O_3 \cdot xNa_2O$ exhibit (29) two resonances: one with large coupling constant, assumed to be due to B atoms bonded to 3 neighboring O atoms; and another with small coupling constant associated with the B atom in a tetrahedral environment. The intensity of the line associated with small coupling constant is proportional to X, showing that the "network modifier" (Na_2O) changes the coordination of the boron atom in the "network former" (B_2O_3).

Certain resonances, such as those of Cl^{35} in $NaClO_3$ or paradichlorbenzene, are so strong that it has been profitable to see how they could be made weaker by dissolving impurities (30, 31) or by irradiation (32). Analysis of such experiments usually proceeds as follows. The impurity centers are assumed to so materially alter the field gradient at all nuclei within a radius R that the resonance is shifted outside of the observed line width and therefore not seen. Let there be n (R) molecules in the sphere of radius R. In order for a quadrupolar nucleus to have an observable resonance it must therefore be at the center of a sphere at least of radius R so that no damaged molecules or impurities are contained therein. If C is the mole fraction of impurity and $1 - C$ the mole fraction of normal molecules; the probability of having n normal molecules around the given molecule is $(1 - C)^n$. This probability would have been unity in the pure crystal and the intensity, I is therefore reduced by this factor: $I/I_0 = (1 - C)^n$.

In experiments in which foreign molecules are introduced into the crystal, C is known and n (R) can be calculated. In $NaClO_3$ n is about 80 and R is 11A. Conversely, knowing n, the mole fraction C of defects can be computed.

Quadrupole resonance frequencies have been detected in several iron group halides (33), e.g., $TiCl_2$ (4.17 Mc/sec.), $TiCl_3$ (7.39), $CrCl_2$ (8.52), $CrCl_3$ (12.812, 12.848), $CrBr_3^{81}$ (85.73). The Cl^{35} frequencies are sufficiently small, compared to the frequency (54.6 Mc./sec.) of atoms, that the bonds are evidently mostly ionic. The quadrupole coupling constant and covalent character increases with the oxidation state of the metal atom, which is a nice confirmation of a general principle of inorganic chemistry. The resonance in the powdered antiferromagnetic halides becomes unobservably broad below the Neel temperature. Use of single crystals would permit a rather detailed mapping of the local order of the spins as a function of temperature.

ELECTRON RESONANCE OF TRANSITION METAL IONS

Resonances of transition metal ions have been studied extensively in dilute (mole fraction $10^{-2}-10^{-6}$) solid solution. At high dilution, broadening due to electron spin-spin interaction is eliminated and the lines in a single crystal become sufficiently sharp to permit the elucidation of the constants of a spin Hamiltonian:

$$\mathfrak{K} = \beta \vec{S} \cdot g \vec{H} + D(S_z{}^2 - \tfrac{1}{3}S(S+1)) + ES(_x{}^2 - S_y{}^2)$$

$$+ \frac{a}{6} \left[S_\xi{}^4 + S_\eta{}^4 + S_\zeta{}^4 - \tfrac{1}{5}S(S+1)(3S^2 + 3S - 1) \right]$$

$$+ \frac{F}{180} \left[35S_\zeta{}^4 - 30S(S+1)S_\zeta{}^2 + 25S_\zeta{}^2 - 6S(S+1) + 3S^2(S+1)^2 \right]$$

The D and E terms vanish if the local environment is strictly cubic, the a and F terms vanish if the electron spin S is less than two. For ions whose spin is 7/2 such as Gd^{+++} (34), or Eu^{++} (35), sixth order terms in the spin components must be added. In the past year, Cr^{+++} has been seen in Al_2O_3 (36), CaF_2 (37), TiO_2 (38), and in MgO (39). Fe^{+++} has been studied in MgO (39), $SrTiO_3$ (40), $BaTiO_3$ (41), $MgWO_4$ (42), Al_2O_3 (43, 44), K_2NaGaF_6 (45), and CdS (46). Mn^{++} has been studied in $KMgF_3$ (47) and in NaCl (48, 49). Some of this work has been qualitative, i.e., to identify the ion impurity responsible for the resonance and to locate it in the unit cell. Much of this research has been motivated by a desire to find a suitable maser material (50, 51). Other work has been directed at the physical meaning of the constants in the spin Hamiltonian. The parameter D for Ni^{++} has been found to vary rapidly with temperature and pressure (52, 53) when it is dissolved in $ZnSiF_6 \cdot 6H_2O$ or in $Zn_3Bi_2(NO_3)_{12} \cdot 24H_2O$. On the other hand, the D for Cr^{+++} (54) was not so temperature dependent in $Zn_3Bi_2(NO_3)_{12} \cdot 24H_2O$. Most suggestive is the observation that at $4.2°K$. D changed from -0.129 cm.$^{-1}$ in going from $(Zn,Ni)SiF_6 \cdot 6H_2O$ to (Zn,Ni) $SiF_6 \cdot 6D_2O$ (53). In the hydrates at least the source of D lies in reasonably small distortions in hydrogen nucleus positions. Further confirmation of this view comes from the observation that D is much less sensitive to pressure and temperature when Cr^{+++} is in $K_3Co(CN)_6$ than when it is in $KAl(SO_4)_2 \cdot 12H_2O$ (55). Fe^{+++} when dissolved in yttrium gallium garnet $3Y_2O_3 \cdot 5Ga_2O_3$ susbtitutes at both the tetrahedral and octahedral sites. According to theory, the sign of the fourth derivative of the crystalline potential changes between these two sites, but a is positive at both. This confirms the theory that predicts that the fourth derivative of the crystalline potential contributes in second order to a (56).

To be informative, electron resonance experiments are best carried out either on a dilute single crystal or in situations such as a solution where complete motional narrowing prevails. The interesting ion $[(NH_3)_5Co—O—O—Co(NH_3)_5]$ has been identified by its 15-line hyperfine structure (57) in solution, showing that the unpaired electron interacts equally with both Co^{59} $(I = 7/2)$ nuclei. Biscyclopentadienyl vanadium (58) exhibits such a

small V^{51} hyperfine structure ($A = 28$ gauss), that $4s$ hybridization of the unpaired electrons is excluded. Hyperfine spectra have been seen in the benzene soluble complexes

$$M = Cu, Ag, Au$$
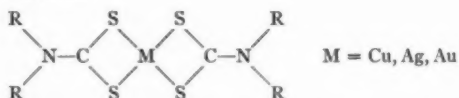
with four lines for $Cu^{63,65}$ ($I = 3/2$), two lines for $Ag^{107,109}$ ($I = 1/2$), and four lines for Au^{197} ($I = 3/2$) (59). The latter resonance is remarkable because it represents the first resonance seen at room temperature in a condensed system containing a heavy element.

If the situation does not permit use of a single crystal or a solution, some information is still available, as has been shown by an electron resonance study of Mn^{++}, Cu^{++}, and VO^{++} absorbed on ion exchange resins, charcoal, and silica gel (60).

Impurities were seen in Group IV elements such as nickel acceptors in Ge (61), P and As donors in Ge (62), N donors in diamond (63), and P and As donors in Si (64). The latter experiment will be discussed in the section on relaxation times. These experiments collectively constitute a landmark in solid state physics; the determination of the distribution of the unpaired electron rests in all cases on the extensively determined hyperfine structures.

ALKALI HALIDES

The alkali halides, simplest examples of ionic crystals, have been widely investigated. Their magnetic resonances are dominated by the effects of quadrupole coupling constants because all the alkali metal nuclei and all the halogen nuclei except F^{19} are quadrupolar. Three types of quadrupolar effects are observed, according to whether the average value of the field gradient, the first derivative of the field gradient with respect to nuclear coordinates, or the second derivative is most important. Crystal imperfections create sufficiently large field gradients at the nuclei of the cubic alkali halides that in general only the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition (almost unaffected by the field gradients) contributes to the observed absorption line. Recently, single crystals of NaI and KI (65) were found to exhibit I^{127} resonances of anisotropic intensity with a sharp maximum when the field is along the 100 direction. Evidently, at this direction the $\pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$, $\pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2}$ transitions collapse into the central transition, which is consistent with the presence of oriented defects such as edge or screw dislocations. At $4°K$., KI (66) exhibits the following anomaly: When the crystal is placed in the field, the nuclear resonance signal reaches equilibrium with a characteristic $T_1 = 560$ min. If the signal is then saturated with rf it subsequently increases to only $\frac{2}{3}$ of its former value with a time $T_1^{sat.} = 213$ min. The anomaly is better understood if one realizes that saturation could not have equalized the population of the $M_I = \pm \frac{3}{2}$ and $\pm \frac{5}{2}$ states in KI, whereas at the beginning of the entire experiment the popula-

tion of all six levels were the same. The shorter relaxation time (which is independent of temperature from $1.5 - 4.2°K$.) must be a cross-relaxation time internal to the spin system and not a true spin-lattice relaxation time.

The effects mentioned that are proportional to the derivatives of the electric field gradient are those associated with nuclear spin-lattice relaxation. Relaxation by the direct process, the conversion of magnetic energy into a single low frequency vibrational quantum, involves the first derivative of the electric field gradient. Relaxation by the indirect or Raman process, in which energy is given up by one vibrational mode and taken by another (whose vibrational quantum differs by a radiofrequency quantum from that of the first), involves the second derivative of the electric field gradient. Inasmuch as the Raman process is dominant except at very low temperatures, only the second derivative of the field gradient can be inferred from the T_1 values. The first derivative has now been obtained by shaking a KI or KBr crystal (driving it with a compressional wave) and measuring the resonant response (acoustic absorption) (67). This experiment, unlike the "pure" quadrupole resonance experiments, is strictly nonmagnetic in nature. The vibrating lattice induces a change in the nuclear spin populations at a rate determined by the square of the first derivative of the field gradient.

The interpretation of the field gradient and its various derivatives is still not perfectly clear. A simple ionic model combined with polarization effects is excellent for the alkali ions but terrible for the halide ions in the diatomic molecules (68, 69). On the other hand, the less exact crystal data in which the ions are further apart can be fitted crudely with a simple point charge model with due allowance for polarizations.

Irradiation of alkali halides has been carried out with x-rays and with neutrons (70, 71) to study the resulting lattice damage. A variety of color centers are observed, such as the familiar F center recently studied in KI (72), LiF, and NaF (73); O_2^- (not produced by irradiation) in the chlorides, bromides, and iodides of sodium, potassium, and rubidium (74); the V_K center (Cl_2^- or F_2^-) (75); and the V_t center is LiF. The latter is a triangular ion F_3^- which has been identified from its F^{19} hfs. in a single crystal (76). When a crystal is irradiated with high levels of irradiation the centers coalesce and pockets of free elements appear in the crystal. In LiF (77) sharp F^{19} and Li^7 resonances were assigned to rotating F_2 molecules and Li metal respectively. In neutron (78) or ultraviolet (79) irradiated LiH both the electron and nuclear resonances associated with the pockets of Li metal are observed; the nuclear resonance exhibited an Overhauser effect (an enhancement of the Li^7 signal when the electron signal is saturated) of a factor of 100 at $4°K$. Li metal prepared in this way has a longer T_1 and is presumably purer than samples prepared in other ways.

NUCLEAR RESONANCE IN METALS

The nuclei of metals exhibit a large resonance (Knight) shift due to the paramagnetic susceptibility of the conduction electrons. In superconducting

metals the Bardeen, Cooper, Schrieffer (BCS) theory predicts that the spins of electrons moving with opposite momentum will be paired, which leads to the value of zero for the spin susceptibility and hence the shift. Actually, in tin (80) and mercury at temperatures below the critical temperature, the shift is reduced but does not go to zero rapidly, as is apparently required. The contradiction has been explained (81 to 83) by correction for the fact that although metallic particles smaller ($10^{-6} - 10^{-6}$ cm.) than the $rf\ H_1$ penetration depth are used, the distances over which the spins of the electrons are correlated are of the order 10^{-4} to 10^{-5} cm. Martin & Kadanoff (84) have proposed another explanation that does not depend on the particle size.

An intense nuclear resonance signal has been seen in zero field in cubic ferromagnetic cobalt at 213.1 Mc./sec. (85). The internal field implied by this frequency is 213,400 gauss, which agrees with values obtained from low temperature specific heats (86) and Co^{60} α-ray anisotropy (87). In an external field, the anisotropic internal fields produced by paramagnetic atoms will produce line broadening. Thus, resonance was detectible in Cu–Mn alloys when the per cent of Mn was greater than 0.1 per cent (88). Actually, the internal field has been shown to be transmitted from the Mn impurity to the copper nuclei via the spin polarization of the conduction electrons; this process is analogous to the mechanism responsible for the proton hyperfine interaction in organic radicals. Systematic studies have been made of the effect of solute atoms on the Cu^{63} resonance in dilute alloys (89).

When the metallic structure is non-cubic, quadrupole resonance can be observed as in indium (90). Quadrupole coupling constants have also been inferred from specific heat measurements at very low temperatures in rhenium (91), gallium, and zinc (92).

A large quadrupole coupling is probably responsible for the failure to observe a magnetic resonance in solid bismuth (93) although the liquid resonance is strong. The line width in lithium is due to magnetic dipole-dipole interactions and it narrows when diffusion correlation times become comparable to T_2. From the pressure dependence of the line width at various temperatures, the activation volume for diffusion in Li has been determined. The activation volume is only 40 per cent of the molar volume, showing that during the diffusion process the lattice must be locally distorted to permit movement (94).

The relaxation time in superconducting aluminum at 0.5–1.4° has been measured by Redfield (95) and Hebel & Slichter (96, 97). As the temperature is lowered, T_1 (0.5 sec.) lengthens until the superconducting phase temperature is reached after which it abruptly decreases to about 0.2 sec. and then slowly lengthens as the temperature is lowered further. The BCS theory (97) explains this effect in detail. In the superconducting state, the formation of the energy gap in the conduction energy level bond at the Fermi surface results in an increased density of states for the levels just below the gap and hence a greater relaxation probability. As the temperature

is further lowered, the density of states near the gap diminishes greatly com-
pared to the density that would exist in the normal metal, so the relaxation
time gradually lengthens. Inasmuch as a magnetic field does not penetrate
very far into the superconducting metal (Meissner effect), one may wonder
how this experiment was carried out. Actually, when the sample was at
equilibrium in a high field and the metal in its normal state, the magnetic
field was suddenly cut off. The nuclei were then allowed to relax for a vari-
able time τ and the nuclear polarization remeasured quickly in a higher field.

A similar technique was used by Anderson (98) to study for the first
time a zero-field nuclear resonance absorption. A sample is observed at a
temperature that assures its relaxation time to be at least of the order of
seconds. While the sample is at zero field for the variable time τ an audiofre-
quency field is applied. By comparing the magnetization of the audio-
treated sample after the field is turned on, with that of a sample to which
audiofrequency radiation was not applied, the absorption of audiofrequency
energy can be determined. Lithium and sodium were found to have the
theoretical line shapes and widths associated with dipolar broadening.
Aluminum on the other hand exhibited a much broader absorption—ex-
tending up to 50 kcps—presumably because of quadrupolar broadening
due to unrevealed strains. Redfield notes that this is a very useful method
for studying quadrupole broadening in cubic crystals.

CHEMICAL SHIFT OF PROTONS

A proton in a liquid in an external magnetic field H_o sees a net magnetic
field (99) $H_n = H_o + H_a + H_b + H_c = H_o(1-\sigma)$ where H_a is the field produced
by the bulk diamagnetism of the liquid, H_b is the field produced by specific
effects of anisotropic neighboring molecules, and H_c is the intramolecular
orbital shielding. Fields H_a and H_b would be negligible in a dilute gas. The
observed chemical shifts σ have been of immense use in determining the
structures of hydrogen-containing molecules (100 to 119). To simplify the
work, a comprehensive tabulation (120) of the range of resonance shifts to
be expected for protons in various groupings has appeared.

A non-empirical interpretation of the chemical shifts is another matter.
The phenomenon depends not only on the ground-state wave function of
the molecule but on its polarization in the external field. Specifically, if Ψ
is the wave function of the molecule in the presence of the magnetic field,
$\Psi = \Psi_o + H\Psi_1 + \cdots$ and the chemical shift depends on both Ψ_o and Ψ_1.
There will not, in general, be a simple proportionality between charge
density and chemical shift for this reason. The diamagnetic shift, being just

$$+\frac{2}{3}\alpha^2\sum_i\left\langle\frac{1}{r_i}\right\rangle,$$

where α is the fine structure constant, and r_i the distance from the electron
i to the proton in units of the Bohr radius, will involve the charge density at
the hydrogen atom but the paramagnetic part will depend on the polarized

part of the wave function. All or nearly all of the paramagnetic shift can be transformed away by changing the origin of the vector potential. Inasmuch as the total shielding is invariant to such a transformation, the diamagnetic shielding must be reduced by the amount of

$$\alpha^2 \frac{R}{3} \sum_i \left\langle \frac{z_i}{r_i^3} \right\rangle .$$

The distance R is half the bond length in H_2 (121) and approximately the O—H bond length in H_2O (122). While the endpoint R will vary, it is generally expected to be close to the centroid of the charge distribution involved in the bond of hydrogen to another element. It may be more fruitful therefore to try to correlate chemical shifts not only with charge densities at the hydrogen atom but also at the atom to which it is bonded.

The preceding comments refer to difficulties involved in the calculation of the field H_e. It may happen that part of this field is of truly long distance origin and a classical approximation may suffice, i.e., we can split H_e into two terms, H_e local and H_e distant. For example, in formamide,

$$
\begin{array}{c}
\text{H} \\
| \\
\text{H} \qquad \text{N} \\
\diagdown \qquad \diagup \quad \diagdown \\
\text{C} \qquad \text{H} \\
\| \\
\text{O}
\end{array}
$$
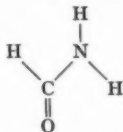
in an inert solvent the local intra- and intermolecular fields at either amide proton may be about the same, but the "distant" field due to magnetic anisotropy of the carbonyl group will be different. Application of the equation

$$\frac{H_d}{H_e} = \frac{\Delta\chi}{3R^3} (1 - 3\cos^2\theta_2)$$

where R is the distance from the carbonyl group to the amide proton, $\Delta\chi$ is the magnetic anisotropy per carbonyl group, and θ_2 is the angle between the CO bond and the line from the proton to the center of the carbonyl group gives reasonable agreement with experiment (123, 124).

Among the many effects of the solvent (125, 126, 127), the most striking are caused by the formation of hydrogen bonds that always tend to unshield the proton. Sometimes hydrogen bonding molecules such as phenols and alcohols are dissolved in non-polar solvents such as CCl_4 and the nature of the polymerization is inferred from the variation of shift with dilution (128, 129). Phenol and t-butanol have been shown to form trimers (presumably cyclic). A variation is to study the competition of hydrogen bonds between solute molecules and between solute and solvent molecules, e.g., H_2O in cyclic ethers or pyridine (130), alcohols and phenols in dioxane and pyridine (131), H_2O and CH_3OH in acetone and dimethylsulfoxide (132), carboxylic acids in acetone and acetonitrile (133), and nitrate ion in anhydrous nitric acid (134).

The hydrogen peak of $CHCl_3$ becomes more shielded when it is dissolved in benzene. The shielding is thought to come from the diamagnetic anisotropy of benzene and a specific interaction that places the proton of $CHCl_3$ along the six-fold axis of the benzene molecule. $SiHCl_3$ exhibits the same effect (135) as do $CHBr_3$ and CHI_3 (136) and the effect is even larger when naphthalene is used as a solvent. If there were no correlation of proton position with aromatic plane the effect would average to zero. If there were a correlation, but with just as many protons at any one angle as at another, line broadening would result. Suspensions of very fine graphite particles have been shown to broaden the water resonance (137). The graphite particles rotate only very slowly and water molecules will be subjected to different fields depending on their position with respect to the particle. The particles must be large enough that the water molecules can not appreciably change their position with respect to the particle in a time associated with the line width. Diphosphopyridine nucleic acid, which is thought to consist of double helices with parallel layers of pyridine and pyrimidine bases, also broadens the water resonance without changing T_1.

Hindered protons like the equatorial protons in cyclohexene (138) or those in hindered methyl groups (139) are shifted compared to unhindered protons. A study has been made of the protolysis kinetics in methanol and ethanol as a function of pH (140). A systematic attempt has been made to understand (phenomenologically) the effect of hindered rotation in substituted ethanes on the spectrum (141). Advantages of a spherical sample (142) and a thermostated probe assembly (143) are discussed by their developers. A convention has generally been adopted to quote chemical shifts in dimensionless form as parts per million (independent of the apparatus used) rather than in field or frequency units which are not directly comparable—in general—between different apparatuses.

Space permits only brief mention of a set of very interesting experiments on chemical shifts of elements other than hydrogen, namely B^{11} (144, 145, 146), C^{13} (147), N^{14} (148), F^{19} (149 to 153), Co^{59} (154), I^{127} (155), Tl^{205} (156, 157), and Hg^{199} (158).

Nuclear Spin-Spin Couplings

Except where chemical shifts are large compared to spin-spin couplings, it is necessary to solve a number of secular equations to derive the values of nuclear spin-spin coupling constants A from spectra. Computations have been made for systems such as $A_p B_q$ where p is one (159) or two (160), ABX_2 (161), ABX_3 (162), and ABC (163). Enough spectra have now been analyzed (164 to 168) to permit generalizations which are given in Table I.

In contrast to the chemical shift, nuclear spin-spin couplings are not sensitive to the solvent (169). They are quantities that depend on the ease with which the magnetic moment of a nucleus can spin-polarize the electrons and have the spin polarization propagate through the molecule and interact with another nuclear moment some distance away. In the approximation of

TABLE I
Spin-Spin Couplings (c.p.s.)

One Bond	H—H	282
Couplings	H—B^{11}	(81–176)
	H—C^{13}	(120–248)
	H—N^{14}	80
	H—F	653

Long Range	(CH$_2$ structure)	Steep function of bond angle ± 2 to 20
Couplings	H—C≡C—H	9.1
	HRC=CHR^1	5–11 *cis* 13–18 *trans*
	X$_1$X$_2$CH—CHX$_3$X$_4$	1–3.5 *gauche* 6–8 for X$_3$=X$_4$=H 10–18 *trans*
	(C—C—C with H)	0 if both C—C bonds are single 0.3–3 if one C—C bond is double 3 if one C—C bond is triple 6–8 if both C—C bonds are double

A_{HX} in the table have been multiplied by g_P/g_X to make them comparable with the proton-proton spin couplings.

perfect pairing, in which every atom is bonded to its neighbors by a unique electron pair bond, this spin polarization can transmit an interaction between two nuclei only if their atoms were bonded to each other. The largest A's are indeed those between two directly bonded nuclei and the long range spin-spin couplings are inherently two orders of magnitude smaller.

Perfect pairing is therefore an excellent first approximation that must be abandoned if one wishes to compute the very small long range couplings. Their values show striking dependence on bond angles and on the number and nature of intervening bonds between the interacting nuclei. The dependence on bond angles of the CH$_2$ (170, 171) coupling has been explained theoretically by Karplus and co-workers. The CH$_2$ system was approximated as a four-electron system and the only wave functions used were the two hydrogen 1s functions H$_1$, H$_2$ and the two carbon hybrids C$_1$, C$_2$. The valence bond structures taken were:

$$\psi_1 = (C_1, H_1)(C_2, H_2)$$
$$\psi_2 = (C_1, C_2)(H_1, H_2),$$

where the symbol (A, B) stands for a valence bond between functions A and B. It is the structure ψ_2, which corresponds to a long bond between the two hydrogen atoms, that is responsible for the spin-spin coupling constant. While the coefficient in the ground-state wave function of ψ_2 is quite small, only by its means can proton 1 communicate with proton 2. The deviation from perfect pairing expressed by the coefficient of ψ_2 varies with the HCH bond angle because the exchange integrals connecting the different electrons vary with angle. The theoretical and experimental coupling constants are large for tetrahedrally bonded carbon atoms (angles near 109.5°) and small for trigonally bonded carbon atoms (angles near 120°). For sufficiently large angles the coupling is predicted to become negative but the exact angle cannot be predicted with certainty. The dependence on dihedral angles of the

$$ \begin{matrix} H & & H \\ & \diagdown \quad \diagup & \\ & C{-}C & \end{matrix} $$
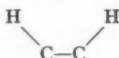
couplings was also explained (172) by valence bond theory; A's are predicted to be positive for all angles.

The sign of the one-bond coupling is clearly positive but the sign of the long range couplings is not *a priori* obvious. Indeed, if the interaction is transmitted mainly through the π-electron system, the sign of the coupling constant (173) is predicted to alternate, i.e., meta coupling constants will have the opposite sign from A's between hydrogens *ortho* and *para* to each other. In substituted benzenes it is found (174) that *ortho* coupling constants lie in the range 8 to 9.5 c.p.s., meta 2 to 3 c.p.s., and *para* couplings 1 c.p.s. or less. (These values are consistent with those for aliphatic compounds given in Table I.) The experimental results with regard to the signs is not simple. First, only relative signs of A's can be obtained from the high resolution spectra. Second, the data in a polyene appear to be different from those in benzenes. Specifically, in the dimethyl ester of muconic acid,

$$ CH_3OOC{-}\underset{H_\alpha}{C}{=}\underset{H_\beta}{C}{-}\underset{H_\gamma}{C}{=}\underset{H_\delta}{C}{-}COOCH_3 $$
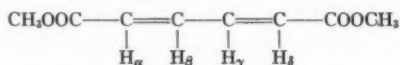
it is found that (175) $A_{\alpha\beta} = 11.8$ cps., $A_{\alpha\gamma} = -1.3$ cps., $A_{\alpha\delta} = \pm 1.3$ cps., and $A_{\beta\gamma} = 11.3$ cps. It has also been shown that in Hg^{199} $(CH_2{-}CH_3)_2$ (176) the couplings $A_{Hg-\alpha H}$ and $A_{Hg-\beta H}$ are of opposite sign.

The chemical shifts between various positions in substituted benzenes are surprisingly small (177, 178) and it is therefore difficult to extract coupling constants. Recently, there has been much interest in the heterocyclics, particularly furans, pyrroles, and thiophenes (179 to 184). The shift between α and β positions was greatest in furan and least in thiophene. A detailed study of thiophenes (185) gives the following results for the spin-spin coupling constants.
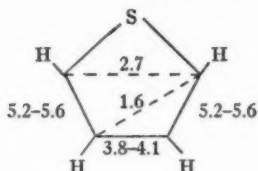
The *ortho* (*cis*) coupling constants are abnormally low compared to the values found in benzenes. For furans and pyrroles they are smaller still. A similar anomaly was noted in bicycloheptadiene (186). These data and those on the bottom of Table I suggest that the π system has a profound effect on many coupling constants.

Miscellaneous theoretical work included calculations of the N—H coupling constant in $N^{15}H_2D$ (187), the F—H and H—H coupling constants in fluorobenzene (188) by molecular orbital methods, and the H—D coupling constant by a variation method (121). C^{13}—H splittings have been shown to lie in the ranges 120 to 132, 154 to 174, and 248 to 251 c.p.s. if the hybridization of the carbon atom was sp^3, sp^2, and sp respectively (189, 190). The increase in single bond coupling with an increasing s character of the bonding orbital is just what would be expected if the contact hyperfine interaction were the predominant mechanism for spin-spin coupling. The possibilities for determining structure by this observation are substantial.

Organic Free Radicals

The principal development in the past year in ESR (electron spin resonance) of free radicals has been in the irradiation of single organic crystals and measurement of the anisotropic hyperfine structure of the trapped radicals produced. Glycine forms $\overset{+}{N}H_3$—$\overset{\cdot}{C}H$—CO_2^- (191 to 193), malonic acid forms $\cdot CH(CO_2H)_2$ (194) and dimethylglyoxime is said to form dimethylglyoxime anion (195). The malonic acid study is particularly important because it furnished evidence for the theory that the electron spin density at the proton is negative, as had been predicted by McConnell. In fact, only the absolute values of the parameters of the spin Hamiltonian:

$$H = AS_zI_z + BS_xI_x + CS_yI_y = aI \cdot S + \text{anisotropic part,}$$

were obtained from experiment. These parameters, A, B, and C, represent both the anisotropic dipolar and the isotropic proton hyperfine interaction. The former has been evaluated theoretically (196); it is merely the dipole-dipole interaction of a $2p\pi$ electron with the nucleus. The three equations $A = a + A_d$, $B = a + B_d$, and $C = a + C_d$, taken in conjunction with the computed A_d, B_d, C_d, yield $a = -63$ Mc.p.s. This is negative and is just the value for the hyperfine interaction frequency per carbon π electron assumed in interpreting the hyperfine structure of aromatic radicals. The C—H hyperfine

structure was smaller in the glycine radical because the unpaired electron was spread over a larger region, giving rise to hyperfine structure with all the magnetic nuclei in the molecule.

The current theories of spin density were further confirmed by the proton spectrum of diphenylpicrylhydrazyl (DPPH) at 77°K. (197) which consisted of two broad humps with one shifted downfield and the other upfield of the normal proton frequency. Valence bond theory predicts that the hydrogen atoms in DPPH are of two kinds, those bonded to a carbon with a net positive spin density and those bonded to a carbon with a net negative spin density. This unpaired spin density will produce a temperature-dependent sort of Knight shift for a proton and will see a greater internal field (of one sign or the other) the lower the temperature.

Weissman (198) has shown that electron exchange from one ring to the other is fast (compared to 10^{-7} sec.) in the anions of paracyclophanes

$$C_6H_4\!\!-\!\!(CH_2)_m$$
$$(CH_2)_n\!\!-\!\!C_6H_4$$
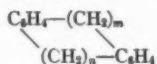
provided n or m is 1 or 2 but is slow if n, $m \geq 3$. Previously, he had shown that there was slow exchange of the two electrons in the biradical
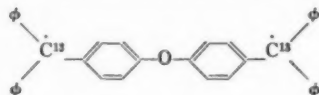
We would like to suggest an explanation for the slow exchange. Presumably in the anion of diphenyl ether, exchange would be rapid as in the first experiment mentioned. An oxygen atom therefore does not act as a serious barrier to the passage of a single electron, but is a formidable barrier to the simultaneous passage of two electrons of parallel spin. The electrons cannot leak through independently since, at least until there was a reverse leak, one part of the large molecule would be positive and the other negative; this would cost too much energy. (There is no analogy here with the structures $H- H+$ and $H+ H-$, which stabilize the hydrogen molecule.) The two electrons with parallel spins have an additional repulsion between them, demanded by the Pauli principle, and therefore have an extremely small probability of being found together in excited orbitals of the oxygen atom. Otherwise put, the barrier to simultaneous tunnelling is too high. This qualitative result would not be given by the common molecular orbital wave functions which, in spite of their other virtues, are seriously deficient in representing electron correlation.

It has been understood for some time that a solution of an organic radical (or an S-state ion) would exhibit a set of narrow hyperfine lines at high dilution ($<10^{-3}$ M), a broad line at intermediate concentrations, and a sharp line at high concentrations. The sharp hyperfine lines are associated with the fact that the lifetime of both the electron and the nuclei in their given spin

states are long. The narrow line at high concentration results because the electron sees the field from so many nuclei that the probability of its seeing any net average nuclear field is negligible. Intermediate broad lines are due to the jumping of electrons from one molecule to another at a rate comparable to the width of the hyperfine components. This rate depends on the electron exchange frequency and the rate of molecular encounters. The latter depends on the concentration and also on the temperature. This, then, is the simple explanation (199) of some apparently anomalous results that showed, for a fixed concentration, that lowering the temperature resulted in increased resolution of hyperfine structure (200).

Other radical work included theoretical studies of $CH_3\cdot$ (201), triplet states (202, 203), H_2^+ (204), and experiments on gaseous H atoms (205), gaseous O atoms (206), $NO(SO_3)_2^=$ (207), hydrogenation catalysts (208), on aliphatic radicals produced by irradiation (207 to 215), and aromatic free radicals (216 to 231).

RELAXATION TIMES AND NUCLEAR POLARIZATION

An ensemble of spin systems with equally spaced energy levels comes to equilibrium with the lattice with a unique, spin-lattice relaxation time T_1. This apparently trivial result is only true because spin-spin interactions (mutual spin flips) mix the populations of such a set of states in a short time T_2 with conservation of internal energy of the spin system. As soon as the level spacing of the individual spins are made unequal, mixing becomes slow and a variety of relaxation times will govern the system. A set of levels can be made equal by changing the magnetic field on a single crystal (Cr^{+++} in Al_2O_3) (232) or by rotating a crystal whose level spacings are anisotropic ($NaNO_3$) (234).

Abragam & Proctor (233) and Bloembergen and co-workers (235) have inquired more deeply into the mixing process. Consider the two-spin system LiF in a strong magnetic field. For arbitrary initial conditions in the spin system, after times T_{2Li}, T_{2F}, there will be a Li^7 spin temperature, a F^{19} spin temperature, and a lattice temperature, which may all be different. What will be the temperature of the dipole-dipole interaction energy? It does not seem that such a temperature can be defined unless both spin systems are in equilibrium with each other, in which case its temperature would be the common spin temperature. The time for establishment of equilibrium between the Zeeman energy and the dipolar energy is called T_{21}; it is physically interesting if $T_1 < T_{21} < T_2$. This condition will prevail for long T_1 when the level spacings of a single-spin system or of a two-spin system are made nearly equal, which means such that the difference in energy between two level spacings is comparable to the dipole-dipole interaction energy. In the example of LiF the separate spin systems will come to equilibrium with the dipole-dipole energy and hence with each other at an appreciable rate when the external field is reduced below 100 gauss (not very large compared to the fluorine line width).

The cross relaxation rate involves a direct exchange of Zeeman for dipolar energy and also an indirect ("Raman") process. In the latter case, one spin loses a Zeeman quantum, another spin gains a Zeeman quantum (of slightly different frequency) and the energy difference is taken up or lost by the dipolar energy. The double spin flips will be important only for systems with rather long T_1's, which usually means the use of liquid He temperatures.

For Cr^{+++} in dilute solution in Al_2O_3, T_1 is 0.1 sec. at 1.4°K. and is presumably governed by spin orbit interaction. Phosphorus-doped silicon has been found by Feher & Gere (236) to exhibit an extremely long relaxation time from 1–4°K. The unpaired electron associated with the phosphorus donor moves so slowly in such a large s-like orbit that its spin-orbit interaction is essentially nil. For P in dilute solution in Si, T_1 is 3000 sec. at 1.3°K.

The long electron relaxation times can be turned to practical use in nuclear resonance experiments by the production of an ensemble of polarized nuclei. The solid state effect (237) is obtained by applying a frequency ν_e $\pm \nu_n$ to a sample where ν_e and ν_n are the electron and nuclear Larmor frequencies respectively. The transitions $\Delta M = +1 \Delta m = \pm 1$ are driven, and an excess of nuclei are placed in the upper or lower spin states. Polarization and hence signal enhancements of 200 were observed for Si^{29} in P-doped Si (238), and 30 for Al^{27} in Cr^{+++}-doped Al_2O_3 (239). These experiments were remarkable from the point of view of technique because a nuclear resonance coil had to be inserted into a microwave cavity.

Systems of $^1S_0$ atoms with nuclear spins are attractively simple. Nuclear magnetic resonance has been seen in mercury gas at low pressures (240); the nuclear polarization was produced by irradiation with circularly polarized Hg 2537 A light ("optical pumping"). It is found that Hg^{201} ($I = \frac{3}{2}$) atoms have a line width extrapolated to zero light intensity of 8 c.p.s.; the width of the Hg^{199} ($I = \frac{1}{2}$) resonance, similarly extrapolated, was less than one c.p.s. For Hg^{199} at $-20°C.$, T_1 is 2 sec.

The past year has seen a thorough exploitation of the Hahn-Carr-Purcell technique for measuring diffusion coefficients, D. This spin-echo technique makes use of the fact that if a system of nuclei is placed initially in phase in a magnetic field gradient, phase coherence will be lost by the migration of nuclei of one Larmor frequency to different points in space where different Larmor frequencies prevail. The diffusion constant (241) for He^3 increases only slightly with temperature in the range 0.5–3.0°K., showing that it is not activation-controlled as in ordinary liquids. On the other hand, for dilute solutions of He^3 in He^4, the diffusion coefficient changes from about 10^{-3} to 10^{-5} cm.^{2}/sec. as the temperature increases from 0.5 to 2.0°K. In other words, the superfluid component of liquid He^4 below its transition temperature does not impede the motion of He^3 atoms. T_1's for He^3 are still in dispute (242, 243).

Self diffusion coefficients have been measured by spin echoes in normal liquids such as water and hydrocarbons, both short chain (244) and long

chain (245). For small hydrocarbon molecules, pressure and temperature dependence of D showed that the activation energies were 10 to 20 per cent of the vaporization energies and the activation volumes were 10 to 20 per cent of the molar volumes. For long-chain hydrocarbons C_nH_{2n+2} the equation $D = K(T)n^{-5/2}$ was found, which shows that the activation energy is independent of chain length.

Previous work on the effect of paramagnetic solutes on proton resonance of H_2O was continued (246 to 249). Most novel were the effects observed on the O^{17} resonance in H_2O. Gd^{+++} produced a diamagnetic shift of 0.53 $\times 10^{-3}$ per mole/l. of Gd^{+++} (250). This means that the O^{17} nucleus is seeing a negative spin density. This could be accounted for by a physical transfer of charge from the oxygen lone pair to an empty orbital on Gd^{+++} (251). Electrons with spin parallel to the Gd^{+++} electrons are transferred preferentially, leaving a net density of electron spin pointing the other way. The adjacent Gd^{+++} may be able to spin polarize the oxygen 1s and 2s shells without the occurrence of any charge transfer, however. Transition metal ions broaden the O^{17} resonance but to an extent that varies with the ion. $CrCl_3$ solutions exert very little broadening effect. Because it is known that the lifetime for attachment of a Cr^{+++} to a H_2O molecule is very long (about a day), it is inferred that broadening is ineffective unless the H_2O molecule is directly attached to the ion. The rate at which the O^{17} spin is turned over by the paramagnetic ion $1/T_2$ is equal to the rate $1/\tau$ at which it can enter the first hydration sphere times the fraction f of oxygen atoms in the first hydration sphere, i.e., $\tau = T_2 f$. This equation assumes that the O^{17} spin is invariably turned over when it is connected to the ion. If this is not true, then experimentally one has found only an upper limit to the mean time τ in which a water molecule is bound. For Fe^{+++} as an example $\tau = 10^{-8}$ sec.

Important developments in double resonance have not been covered in this report. This is partly because two excellent summaries have recently appeared. The proceedings of a conference on this subject held in Paris, 1958, have been printed (252). The papers given at a conference on optical pumping held in Ann Arbor, Michigan have been prepared in mimeographed form (253). The successful application of the optical pumping techniques to the detection of electron resonances in solids has been reported by Geschwind *et al.* (254, 255). Resonance was observed at 4°K. on an optically excited state of Cr^{+++} in Al_2O_3. For a long time optical and microwave spectroscopists have performed experiments on solids containing paramagnetic ions but correlations of the results of the two types of experiment have been rare. Now it will be possible to study the effects of optical absorption on magnetic absorption and vice versa; it will be easier to identify spectra of unknown "centers."

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COMBUSTION AND FLAMES[1,2]

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Introduction

In combustion research, as in other fields of applied science, it is often helpful to differentiate between three essentially distinct categories of endeavor, namely (a) fundamental research designed to clarify basic principles involved in flame processes, (b) applied research that is motivated by the urgent need to solve a practically important problem, and (c) research of an intermediate character that is not likely to aid in the solution of a practically important problem and also does not provide new basic insight into combustion mechanisms. In combustion research, as perhaps in no other field of science, the investigator must continuously guard himself against the ever present temptation to invent a problem that requires extensive studies for proper comprehension but is ultimately neither illuminating nor useful.

Basic Theoretical Research in Combustion

All combustion processes involve chemical changes in flow systems. The fundamental ingredients of the science are therefore composed of (a) the conservation equations for multicomponent, reacting gas mixtures; (b) explicit introduction of appropriate sets of rate laws for gas-phase and surface-catalyzed reaction rates; (c) imposition of suitable initial or boundary conditions; and (d), what is perhaps most difficult to accomplish in a meaningful manner, the mathematical formulation of a tractable problem that contains the essential features of the physical processes under study.

Satisfactory kinetic theory formulations for the conservation equations in reacting gas mixtures have been given by Chapman & Cowling (1) and by Hirschfelder and his collaborators (2). The continuum theory approach is less transparent (3, 4) although it has recently been shown by Nachbar, Williams & Penner (5) to yield results equivalent to those derived from the kinetic theory of gases.

Formally, the problem of estimating transport properties in reacting gas mixtures is well understood, although significant uncertainties remain in any given case in so far as appropriate estimates for interaction potentials and effective collision cross sections are concerned. This last statement is particularly true for free radicals and excited atoms or molecules of the type that is likely to occur in regions of active combustion.

Combustion processes involve all of the uncertainties that are imposed by incomplete knowledge of chemical reaction rates. The numerous publications in this field will be mentioned in the following discussion only if they have a direct bearing on the flame processes considered by us in detail. Nevertheless, it is important to note that some specialists in combustion favor the opinion that basic research in combustion is essentially synonymous with the elucidation of fundamental reaction mechanisms and rates.

Steady laminar flames in premixed gases.—Perhaps the simplest and most fundamental problem in flame theory concerns the theoretical prediction of the steady laminar flame velocity in combustible gas mixtures. The studies of Zeldovich (6), Jost (7), Lewis & von Elbe (8), Hirschfelder *et al.* (9), von Kármán, Penner & Millán (10 to 12), Eyring *et al.* (13), Spalding (14), Emmons (15), and others (16 to 20) have clarified the basic problems to such an extent that general agreement may be said to exist now among active workers in this field concerning proper methods for formulating the differential equations, associated boundary conditions, and efficient procedures for solving the basic set of differential equations either numerically or by approximate (semi-) analytical techniques. The steady-state assumptions for the chain carriers (10) may often be used to advantage in deriving first approximations to the flame speed (10 to 12) although detailed composition profiles are not usually predicted correctly (21 to 23). The principal errors in laminar flame theory result from the lack of knowledge concerning chemical reaction mechanisms and rates and, to a lesser extent, from errors in the estimates of the transport parameters. In spite of observed large deviations for selected chemical species in excited states, it must be concluded from the apparent successes of laminar flame theory that the use of local average properties (e.g., temperature, velocity distribution, etc.) constitutes an acceptable approximation.

Detailed analytical studies by Montroll & Shuler and their collaborators (24 to 27) of relaxation processes for selected emitters in excited states provide some insight into the nature of the persistence of anomalous rotational and vibrational temperatures (28 to 31). This fascinating subject is, however, beset by experimental and analytical difficulties in practically important flames. It is unrealistic to expect that early advances in this field will lead to a proper foundation for a truly molecular theory of combustion in which significant differentiation is introduced not only between chemical species but also between specified chemical reactants with either different translational energies or effective population temperatures or both.

Homogeneous and heterogeneous diffusion flames.—A significant number of flame problems can be understood, in good approximation, on the assumption that the chemical reaction rates occur rapidly as compared with the transport of mass and energy. This concept has been used with good success in homogeneous systems and also in heterogeneous (e.g., two-phase) systems (32 to 37). The demonstration (38 to 41) of the practical utility of the diffusion-flame approximation in some liquid-fuel rocket engines suggests

the possibility of developing rational scaling procedures for these devices (42, 43). Of considerable fundamental importance is the development of a statistical theory of spray combustion by Williams (44 to 47) using the diffusion-flame approximation.

The detailed description of diffusion flames is far more advanced for laminar processes than for the practically important turbulent reactions. Nevertheless, useful progress (48) has also been made in the latter field, particularly because of the utilization of appropriate dimensionless groups for correlating and extrapolating available experimental data.

A simplifying approximation that has been employed extensively in recent theoretical studies on flames, particularly diffusion flames, is the Shvab-Zeldovich procedure (49 to 51) in which the kinetic theory estimate of unity is introduced for the dimensionless ratio (i.e., the W. K. Lewis or Lewis number) measuring the relative energy transport by thermal conduction and by diffusion. With this assumption, the local energy in a reacting gas mixture becomes independent of the occurrence of diffusion and heat conduction. Furthermore, the equations for the conservation of the individual chemical species become similar with each other and with the energy equation in such a way that (partial) solutions may be found that are independent of the generally poorly-understood specific reaction rate parameters. Applications have been made of this procedure in the solution of such diverse combustion problems as the burning of single fuel droplets (51) or of statistical distributions of droplets in an oxidizing medium (44), ignition and combustion in a laminar boundary layer (52 to 55), constant-volume explosions (56), laminar flame propagation (10), etc.

Burning of monopropellant droplets.—The burning mechanism of monopropellant droplets involves over-all rates that are controlled by both chemical reaction rates and by transport processes. Significant theoretical solutions to this important problem have been obtained by Williams (44, 47) and by Millán & Sanz (57). A numerical solution for the burning of single monopropellant droplets was obtained earlier by Lorell & Wise (58).

Ignition of premixed gases.—A very useful empirical correlation formula has been developed for minimum ignition energies in premixed gaseous systems. Early interpretation by Lewis & von Elbe (59) of the empirical results in terms of an "excess enthalpy principle" must be revised since the "excess" enthalpy has been shown to be either positive, negative, or zero depending only on the numerical value of the effective Lewis number (60 to 62).

Ignition processes seem to involve the requirement that the minimum energy supply is equivalent to the energy required for steady propagation of the flame (62, 63). This fundamental idea is in accord with results observed in many homogeneous and heterogeneous systems. A more elaborate theory of ignition has been discussed by Rosen (64). Some interesting recent experimental studies on ignition have been performed by Wolfhard (65).

Flammability limits.—Following the introduction by Spalding (66) of the

idea that flammability limits are determined by heat losses from a combustion zone, a more transparent analytical treatment has been worked out by von Kármán (67). Mayer (68) has succeeded in presenting this approach in a form which is really useful for the correlation of experimental data.

Turbulent flames.—In view of the enormous difficulties involved in the quantitative description of turbulent processes without combustion, it is not surprising to find that progress in our understanding of turbulent combustion flames has been very slow. The early work of Scurlock & Grover (69) and Karlovitz (70) appears to be beset with conceptual and interpretive difficulties that include even experimental uncertainties (71) concerning the existence and magnitude of flame-generated turbulence. However, Kovaszny (72) has recently proposed a simple and useful approach, at least to the phenomenological description of turbulent flame processes, which appears to find immediate applications in the interpretation of measured turbulent flame velocities. Extensive studies on turbulent flames have been described at a recent international symposium (73). Translations of representative Russian papers in this field have also become available (74). Spectroscopic studies on turbulent flames and their proper interpretations are still a somewhat controversial problem (75, 76).

Chemical reactions in supersonic flow.—With the current interest in the development of high-Mach number ramjets, as well as with long-standing studies on rocket nozzle and exhaust flows, there has recently been considerable interest and activity relating to chemical changes in supersonic flow. Clever experimental arrangements have been devised by Behrens & Rössler (77), Nicholls *et al.* (78, 79), Gross *et al.* (80, 81), and others (82 to 85). However, little progress has been reported on the quantitative interpretation of results although there is no basic uncertainty about the proper utilization of characteristics calculations in supersonic flows with heat release.

Detonation phenomena.—There is probably no part of combustion research in which more careful measurements or more careful interpretive work has been done than on detonation phenomena. This work covers the entire spectrum of activity: steady propagation velocity measurements in order to verify or disprove the existence of Chapman-Jouguet detonations by Kistiakowsky *et al.* (86 to 89); related theoretical studies by Kirkwood & Wood (90, 91), Hirschfelder *et al.* (89, 92 to 94), and others (89, 95 to 102); measurements of detonation induction distance (89, 103); two-dimensional phenomena by Fay *et al.* (104 to 106); gas-dynamic or phenomenological interpretations by Oppenheim (102, 107); spinning detonations by Chu (108); transitions from deflagration to detonation (89, 103); spherical detonations (89, 109, 110), etc. A brief look at the literature indicates that none of the interesting phenomena associated with detonations, other than the thermodynamic procedure for calculating steady detonation velocities at the upper Chapman-Jouguet point, has proven amenable to unambiguous and unimpeachable analytical interpretation.

Constant volume explosions.—Starting with the concepts of thermal and branched-chain explosions, which were perhaps first clearly defined by Semenov (111), slow but significant progress has been made in the quantitative description and interpretation of many chemical processes. We refer to a series of recently published books for detailed discussions of these important problems (8, 89, 111).

Unsteady flames.—Many interesting flame phenomena are not adequately described by the steady-state fluid-dynamical equations together with appropriate reaction terms. In this connection, we have already noted briefly recent work on ignition and on the transition from deflagration to detonation. Other interesting phenomena are connected with vibratory motion, e.g., cellular flames which appear to depend on preferential diffusion of light and heavy constituents [Markstein (112) and others]. Non-steady flame phenomena have also been discussed by Rosen (113), Jost *et al.* (114), and others. A comprehensive review of this subject is currently in preparation (115).

Thermochemical research.—No discussion of flames is adequate without some consideration of related thermochemical studies which, in principle, define at least the final equilibrium state after completion of combustion. Interest in exotic propellants has led to renewed basic studies on compounds containing such elements as F, B, Be, Cl, Li, Si, etc. (116 to 120). Significant uncertainties remain at the present time even with regard to the proper standard heats of formation for many important oxides of light metals. Although the experimental and theoretical procedures used for studies of this type may be said to be classical, there is little doubt that continued work, particularly on high-temperature thermodynamics, will constitute an integral part of present and future combustion activities.

Ionization in flames.—No modern discussion of experimental and theoretical studies concerned with combustion problems is complete without mention of ions and electrons in flames (121 to 128). The weight of available experimental evidence suggests the prevalence of "excessive" degrees of ionization in flames when a comparison is made with the corresponding calculated equilibrium data. This phenomenon of "chemiionization" must be directly related to the elementary processes producing ions and electrons in flames and may therefore be appropriately classified as a special branch of (high-temperature) reaction kinetics.

SELECTED COMBUSTION PROCESSES MOTIVATED BY CURRENT DEVELOPMENT STUDIES

One of the most difficult tasks facing the specialist in combustion involves the proof that the results of basic research have a more or less direct bearing on the development or production of any type of combustion device. In so far as the authors are able to judge, the results of combustion research can often be shown to clarify important concepts, to provide broad guide lines for development procedures, and to facilitate the qualitative prediction

of new performance results or the semi-quantitative correlation of available data. However, combustion research has not proved to be directly useful in the solution of important practical problems that have arisen as a direct consequence of engine development studies. We proceed to demonstrate the validity of this last contention by examining four troublesome development problems that have provided direct motivation for a great deal of combustion research. Although interesting results have been derived from these studies, the practical problems have certainly not been solved or even ameliorated by the use of research results.

Combustion and ablation in boundary layers.—In connection with the design of nose cones for reentry studies on intercontinental and shorter range ballistic missiles, a great deal of basic work has been done on heat transfer through hypersonic boundary layers with and without combustion (129 to 154). Comprehensive reviews of this work have been published by Lees (130), Allen (131), Stalden (132), Griffith (133), and Rosner (134).

Because of large aerodynamic heating rates at hypersonic speeds and the low heat capacity of sharp-nosed bodies, interest has centered on blunt-nosed bodies and the heating rate at the stagnation point. Of particular interest are studies on the heating rates with recombinations of atoms. Lees (143) and Fay & Riddell (152) have presented solutions to the problem employing the assumption of a binary mixture of atoms and molecules. For the case of chemical equilibrium, their results have been substantiated by shock tube experiments performed by Rose & Stark (151) and by Rabinowicz (139). The assumption of a fully catalytic wall, corresponding to zero atom fraction at the surface but with finite recombination rate, employed by both of the aforementioned authors was questioned and investigated further by Scala (146) and Goulard (140). They showed that the atom fraction at the wall could be small but never zero. The case of arbitrary catalytic activity at the wall has been studied by Rosner (136), Chambré & Acrivos (153), and others. The catalytic activity of specific metallic and ceramic surfaces for atom recombination has been investigated by Linnett & Marsden (154). Rutowski (149) has considered the stagnation point heat transfer for ionized gases.

The theory for ablation of surfaces subjected to aerodynamic heating has been developed by Bethe & Adams (155) and others (156 to 161). The analytical studies developed by Lees (156) and Roberts (157) started with an assumed velocity profile whereas Bethe & Adams assumed the form of the temperature profile. Carrier (159) has improved the analyses. A comparison of these theories has been given by Sutton (160). Apparently all of the theories yield heating and melting rates that are too high.

While theoretical and experimental shock-tube studies were in progress on hypersonic flow over bodies of various shapes, experimental flight tests were, of course, also performed. These flight tests have shown that a blunt, ablating nose cone that serves as a heat sink can be constructed in such a way that it is able to withstand the heat transfer and thermal stresses following almost any missile trajectory.

Chemical changes during nozzle flow.—The theoretical performance differences for rocket engines between nozzle flow without composition change (i.e., frozen or constant-composition flow) and nozzle flow with maintenance of complete chemical equilibrium (i.e., "shifting" or equilibrium flow) are known to amount to from 2 to perhaps 15 per cent depending on the propellant composition and on the adiabatic flame temperature. For conventional, low-energy propellants (i.e., propellants with a specific impulse I_{sp} of less than about 250 lb. thrust-sec./lb. mass of propellant) the theoretical performance differences are relatively small; however, for high-energy propellants (i.e., I_{sp} of 275 to 400 sec.) the larger performance differences are encountered. A change of a few seconds in specific impulse for a long-range missile of conventional design generally corresponds to range differences of hundreds of miles.

Because of the numerical complexities of an exact solution of the one-dimensional nozzle-flow problem with chemical reactions, various approximate procedures have been developed. Early work by Penner (162 to 164) yielded criteria for near-equilibrium and near-frozen flows. More recently, Bray (165), employing Lighthill's (166) ideal dissociating gas and Freeman's (167) rate parameter, has investigated the flow of initially dissociated nitrogen and oxygen through a hypersonic nozzle. He found that the flow could be described by three regions of flow: an initial equilibrium flow, a short transitional region in which there is marked deviation from equilibrium, and finally, an essentially frozen flow. This behavior may also be observed in the complete calculations of Krieger (168) and Heims (169). Based on his study, Bray has proposed an approximation in which the flow is initially in equilibrium and then suddenly freezes, the point of sudden freezing being determined by the rate equations. Wegener, who has observed experimentally the flow of dissociated N_2O_4 in a supersonic nozzle (170, 171), applied Bray's approximation to his data and found good agreement (172).

In spite of the availability of *procedures* for analyzing nozzle-flow problems, few or no useful predictions for real rocket engines are possible because (*a*) reliable experimental data are not available for high-temperature reaction rates of propellant reaction products and (*b*) the theoretical calculations start from the premise that thermodynamic equilibrium has been reached in the combustion chamber. This assumption is unjustified for most propellant systems and, in particular, must be viewed with doubt for high-energy solid propellants. For this reason, the study of refined nozzle calculations with chemical reactions has been of no direct aid in assessing the actual attainable engine performance which must still be evaluated empirically.

Burning rates of solid propellants.—Following war-time studies on the burning rates and decomposition mechanism of double-base propellants by Daniels *et al.* (173), Crawford & Parr (174), Rice & Ginell (175), and others, basic research in this field went through a long period of dormition. Recently, the corresponding problem has been attacked with vigor for composite solid propellants, and simplified model studies have been performed for selected

propellant ingredients and even for specially synthesized composite powders. References and a discussion of this work, including consideration of contributions by Geckler (176, 177), Summerfield *et al.* (178), Friedman *et al.* (179), Nachbar (180), Schultz & Dekker (181, 182), and others, may be found in a recently published survey paper (183). An exhaustive compilation of basic knowledge on solid propellants is in preparation (184).

The diverse theoretical studies on the burning mechanism of composite solid propellants lack a firm foundation because of the sparsity of definitive experimental data. The work of Schultz and colleagues (181 to 183) on pyrolysis rates of pure oxidizers and binders has led this investigator to the conclusion that the mean temperatures during steady burning are different for the oxidizers and fuels. Geckler (176, 177) has been concerned with the formulation and solution of the gas-phase chemical reactions by using models and methods that are analogous to those employed in laminar flame theory. Summerfield and his colleagues (178) have performed experimental studies primarily on ammonium perchlorate propellants and have explored the implications of a "granular diffusion flame model" in which the combustion rate is controlled by both transport processes and chemical reaction rates. Fundamental experimental studies on pure ammonium perchlorate have recently led Friedman *et al.* (185) to the conclusion that radiative heat losses play an important part in determining flammability limits. Various attempts to construct "complete" theories of burning are in progress and will presumably be reviewed at the *Eighth International Combustion Symposium* in 1960.

We may justifiably start from the premise that the objective of basic research on the burning mechanism of solid propellants must be the development of useful, predictive procedures for designing propellants with arbitrary, specified burning rates. However, when viewed with this objective in mind, we must assert categorically that neither the published studies on double-base propellants nor the current work on composite propellants has had, or is likely to have, a profound influence on propellant development. Propellant design and development are done by specialists on the basis of intuitive insight or of artistic notions developed through long experience. The day when propellants can be manufactured to predetermined specifications by the use of scientific principles appears to lie in the distant future.

Combustion of sprays.—Propulsion devices utilizing liquid propellants ultimately involve the burning of sprays. The recognition of this fact has provided the immediate motivation for experimental and theoretical studies on the burning of single fuel droplets (32 to 37) and of droplet arrays (40, 44 to 47) in oxidizing media. These investigations have led to a satisfactory understanding of heterogeneous diffusion flames and to an acceptable first approximation for an analytical description of the phenomenon. Experiments by Kumagai & Isoda (36) on burning droplets in a freely falling apparatus constitute the culminating tests of the theory and have shown that a steady-state theory is, in fact, not strictly applicable.

The task of integrating the knowledge derived from single-droplet studies

into a theory of spray burning has been pursued by Williams (44) who has pointed out the need for developing a statistical theory and who has invented a Boltzmann-type equation in which the individual liquid droplets play the same role as the molecules in the mathematical theory of nonuniform gases. The essential validity of this procedure, if it requires proof, has been demonstrated by quantitative calculation of the (laminar) burning velocity in a monodisperse, dilute spray for which a direct comparison with experimental data is possible.

Application of the theory of spray burning to engine combustion studies presents difficulties of staggering magnitude. To begin with, the effective drop-size distribution and flow velocity in sprays produced by any injector used in an engine are unknown. Such troublesome problems as droplet breakup on collision, droplet generation during burning, etc., are completely beyond our present comprehension of the behavior of heterogeneous systems. Simplified models for the combustion of liquid propellants in rocket engines have been treated by Priem (38), Spalding (186), and Mayer (187).

In view of the impossibility of using the available spray combustion theory for useful predictions, it is only reasonable to consider the possibility of employing the theory as a framework for the correlation of experimental results. A serious test of the theory has been worked out (40) for a diverging liquid-fuel rocket engine with the obvious conclusion that the precision of correlation of experimental data depends only on the number of adjustable parameters employed in the analysis.

Engine Combustion Problems

In addition to strongly motivated research, examples of which have been considered in the preceding section, it is appropriate to mention briefly the representative development problems that are of major importance in connection with current developments of actual (rocket) engines.

Liquid-fuel rocket engines.—Perhaps the single most troublesome and costly problem encountered in liquid-fuel rocket engine development is associated with the uncontrolled development of high-frequency combustion oscillations. Significant progress in unravelling the essential features of this phenomenon has been made by Crocco (188), who has replaced the entire complex combustion processes through a symbolic time-delay step. These results are, however, at the present time more useful for *post mortem* commentary than for *a priori* predictions and elimination of difficulties. For more recent considerations of this controversial problem, we refer to discussions by Zucrow & Osborn (189, 190) and Crocco *et al.* (191, 192).

Another approach for reducing the costly development difficulties was initiated by Penner (43) and Crocco (42) and involves utilization of the principles of similarity analysis for rational scaling of well designed engines to larger sizes. This approach is also of limited utility because maintaining exact similarity with respect to all of the important dimensionless groups is impossible; furthermore, the rate-controlling combustion processes cannot be defined properly, nor is it possible to predict even the changes in over-all

conversion time as functions of injector configuration and motor size. Thus the design of liquid-fuel rocket engines, as well as the scaling to larger sizes, has remained an empirical art.

Solid-fuel rocket engines.—Among the most troublesome practical problems in solid-fuel rocket engineering is the uncontrolled development of resonance burning, i.e., of large pressure maxima that may lead to rupture of the engine or disintegration of the propellant charge. Theoretical studies by Grad (193), Smith & Sprenger (194), Green (183, 195), Green & Nachbar (196), and McClure & Hart (197) have indicated possible causes for this phenomenon. Experiments performed by Brownlee (198) and Price & Sofferis (199) suggest that the phenomenon, though reproducible, is an exceedingly sensitive function of propellant composition, i.e., of combustion rates. Resonance burning is probably also dependent on the elastic properties of the solid and on the coupling between propellant and container walls. Needless to say, the theories that "predict" a discrete spectrum of unstable operating frequencies, as well as the more elaborate and more appealing analyses that suggest continuous regions of instability, have no current impact on the design of propellant charges and contain so many unknown parameters that useful predictions are not likely to be made in the near future.

Air-breathing engines.—The principles of similarity analysis have proved of some value in the design of turbojet combustors (200, 201). Furthermore, studies on the mechanism of flame holding behind bluff bodies (202 to 207) have yielded useful concepts for engine builders although the practical design involves flame spreading in ducts and interference between wakes.

CONCLUDING REMARKS

The preceding examination of the relation between combustion in flames and practical propulsion development leads inevitably to the conclusion that a major stumbling block to understanding and utilizing combustion processes is the lack of information concerning high-temperature kinetics. Combustion research is more likely to be ultimately useful if it is really fundamental and thorough and is less likely to be of value if confined to a specific process or procedure. All good research is justifiable on gas-phase, liquid-phase, and solid-phase kinetics, on transport properties, on mixing in low-velocity and high-velocity streams, on the theory of turbulence, on mass and energy transfer by diffusion, on flame spectroscopy, etc. Much greater circumspection is required, however, in the selection of so-called developmental research: it is so easy to invent a problem and to study the invention and so difficult to construct a meaningful approximation to the real thing!

In the preceding survey we have made no effort to furnish an exhaustive literature summary. For this reason, we present a separate list of specialized texts and symposium proceedings (208 to 231) which should serve as adequate starting material for more complete literature coverage, particularly on experimental problems and on the numerous theoretical topics that we have not treated specifically.

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THE SOLID STATE[1]

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An earlier author of this review remarked that the problem of selection of topics was going to become increasingly difficult with time, because of the large and growing volume of literature pertaining to the solid state. The truth of this is particularly apparent at present. Not only is a large fraction of the pages of such standard journals as *The Physical Review* and *Journal of Applied Physics* devoted to solid state work, but journals have also appeared that are devoted exclusively to solids, and an increasing number of books in the field are appearing, some of which, such as the excellent Seitz-Turnbull series *Solid State Physics*, are devoted to comprehensive reviews.[2] Faced with this problem of selection, the present authors have elected to review several aspects of solid state research that may reasonably be claimed to fall within the range of interest of the physical chemist and are not within the scope of other chapters in this volume. Thus, many topics that are of central importance in "the solid state" but are considered to be primarily "solid state physics" (e.g., electrical, magnetic and optical properties, and electronic band structure) will not be considered. It is freely admitted that this entails a certain arbitrariness of choice.

DIFFUSION

Diffusion processes are of course fundamentally important in many solid state phenomena; these include, for example, precipitation processes, solid state reactions, corrosion, sintering, and the annealing of radiation damage. A large amount of work, both theoretical and experimental, has been done in an effort to understand the basic mechanisms involved in diffusion. In one of the more interesting theoretical studies, Rice (2) has developed a dynamic theory of diffusion by the vacancy mechanism. In effect, this is an improvement on the activated complex treatment of diffusion, and it avoids ascribing well defined thermodynamic properties to the activated state. Rather, the parameters determining the diffusion coefficient, D, are defined in terms of the normal coordinates of the crystal. The effects of lattice imperfections are considered explicitly in formulating the normal mode analysis of the highly correlated atomic motions. An extension of the theory by Rice & Nachtrieb (2a) analyzes the pressure dependence of the diffusion coefficient, permitting a comparison of theory with experimental results for self-diffusion in lead. Nachtrieb *et al.* (3) carried out an extensive experimental investigation of the effect of pressure in this case.

Reiss (4) developed a theory for the influence of substitutional solutes on

[1] The survey of the literature for this article was completed December 1, 1959.

[2] A number of topics in the solid state chemistry and physics of semiconductors have been reviewed in the book *Semiconductors* (1).

self-diffusion, which considers the correlated motions of host atoms, vacancies, and solute atoms in *fcc* lattices. From data on the diffusion coefficient of the solute, and the dependence of the self-diffusion coefficient on solute concentration, the ratio of the jump frequencies for vacancy exchange with a solute and with a host atom in the first coordination shell of the solute can be estimated. A good estimate of the influence of a given solute on self-diffusion can be made knowing only D for the solute. Comparison of the theory with available experimental data was satisfactory. In a particularly interesting experimental study, Watkins (5) used electron spin resonance and dielectric loss measurements to study the two kinds of jump frequencies just referred to. He observed the motion of a vacancy bound to Mn^{++} in alkali chlorides, finding that the vacancy exchanged first with the host cations rather than with the Mn^{++}. Considerations of the lattice distortions around the doubly charged Mn^{++} are consistent with this result.

Penning (6) has calculated the rate of the diffusion-limited disappearance of excess vacancies, with the surface and dislocations in the volume both acting as vacancy sinks, showing that both kinds of sinks are important for reasonable sample sizes and dislocation densities. Damask *et al.* (7) made a machine calculation of the motion and binding energies of mono-, di-, and tri- vacancies in copper. Dienes & Damask (8) studied radiation-enhanced diffusion in solids, comparing experimental data for α-brass with a theory developed to describe the dependence of the enhanced diffusion on radiation flux and diffusion temperature. From this they were able to obtain information about the mechanism by which defects were removed from the lattice. Peterson & Ogilvie (9) observed the increase in D for As in Ge after 2 Mev electron bombardment, estimating a lifetime for the vacancies produced in the bombardment. Elcock (10) considered the mechanism of vacancy diffusion in simple ordered binary alloys. Bullough & Newman (11) gave an improved treatment of the Cottrell & Bilby theory of strain aging by the flow of impurities to dislocations. Shewman (12) studied the "thermal diffusion" of vacancies in zinc, i.e., the development of a concentration gradient in a temperature gradient (the equivalent for atoms of the thermoelectric power for electrons, and well known, of course, in fluids). No net flux of vacancies was observed, indicating a balance between the thermal diffusion force and the effect of the strong concentration gradient.

Brebick (13), in an improvement of the Wagner treatment, considered theoretically the interdiffusion in binary ionic semiconductors, comparing his results with experimental data for PbS. Cuccione *et al.* (14) considered vacancy migration of both anions and cations in alkali halides, estimating values for the energies involved and comparing these with experimental data. Pines (15) studied the mechanism of reactive diffusion in compounds, during which a new phase is produced by chemical reaction.

A large number of experimental studies have provided data on specific systems, which are of interest, but space limitations preclude the mention of more than a fraction of these. Of interest in connection with experimental

studies is the work of Malkovich (16), who analyzed some systematic errors involved in the determination of D, arising from improper consideration of initial and boundary conditions and from insufficient accuracy of experimental quantities. Thomas (17) has made a thorough study of the diffusion and precipitation of In in ZnO. Boltaks and his colleagues have investigated the diffusion oi Sb in Ge (18), the diffusion of impurities and self-diffusion in PbSe and PbTe (19), and the effects of an electric field on the diffusion of Sb in NaCl (20), finding in this case that it diffused as Sb^{3-}. Sturge (21) corrected the previously anomalous D for B in Ge (21). Batdorf & Smits (22) studied the diffusion of impurities in Si while it was evaporating, Logan & Peters (23) the diffusion of oxygen in Si, and Coupland (24) the diffusion of P in Si. Other compound systems investigated include Cu in CdS (25); Zn in InSb (26); Zn and Se in Bi_2Se_3, BiSe, and CdSb (27); oxygen in Cu_2O (28); Ag in Ag_2S (29); and self-diffusion in alkali halides (30).

Among the numerous studies of metals were the effects of torsional strain in the enhancing of self-diffusion in silver, by Lee & Maddin (31), and work on the self-diffusion in silver during plastic deformation by Darby et al. (32) and by Forestieri & Girifalco (33), the latter finding D to be proportional to strain rate over a considerable range of temperatures. Kirkendall diffusion was studied by Balluffi and co-workers (34, 35). Powers & Doyle (36) used mechanical relaxation to measure the diffusion of interstitial solutes in bcc metals.

A very different diffusion problem is concerned with the dynamic stability of frozen radicals. Jackson (37) estimated a critical free radical concentration, such that any greater concentration would be able to ignite spontaneously. For N in an N_2 lattice, this concentration is of the order of 0.3 per cent.

LATTICE DEFECTS

Vacancies.—The study of vacancies in solids has received increasing attention. A considerable number of papers is concerned with vacancies that were quenched in from high temperatures. Valuable information, particularly about the decay of the vacancy content, could be obtained from the study of the electrical and mechanical properties as well as the etching behavior of metals and dielectrics. Before discussing these investigations, the most direct technique of observing point defects should be mentioned. By means of a field-ion-microscope, Mueller (38), in a series of excellent pictures, exhibited individual crystal planes in the form of regular patterns of bright spots. Vacancies were easily visible as dark areas within the exposed lattice plane. In order to determine the vacancy concentration in the bulk of the crystal, Mueller removed lattice planes in successive steps by careful field evaporation. The vacancy concentration is directly given by the number of vacancies observed divided by the number of atoms removed. Knowing the quenching temperature, the energy for the formation of vacancies in Pt was found to be 1.15 ev, in excellent agreement with the value obtained from electrical measurements (39).

DeSorbo & Turnbull (40, 41) investigated the formation and the annealing-out of point defects in aluminum. The specimens were quenched to $-50°C$. since at room temperature vacancies are eliminated quite rapidly, particularly in the presence of a large dislocation density (42). The energy of vacancy formation in aluminum was found to be 0.75 ev. The kinetics of the vacancy motion were investigated in detail. In aluminum of very high purity the rate of vacancy annealing depended on the vacancy concentration and the annealing temperature, but it was independent of the temperature T_i of vacancy injection. In zone-refined aluminum of lesser purity the rate of vacancy annealing depended upon T_i. Two hypotheses for the impurity effects were considered; namely (a) trapping of vacancies at impurity atoms and (b) inhibition of dislocation climb by adsorbed impurities. The energy of generation of vacancies in copper was measured as 1.0 ev by Airoldi et al. (43) for an initial concentration of vacancies of 10^{-5}. The recovery of the quenched-in resistivity was almost complete at annealing temperatures of 350° to 450°C.

Doherty & Davis (44) observed small surface pits on electro-polished surfaces of aluminum single crystals formed during cooling from elevated temperatures. These pits did not form in the vicinity of sub-boundaries or grain boundaries. The formation of these pits during cooling is attributed to the condensation of vacancies at specific locations in the free surface. It is believed that a definite and constant supersaturation of vacancies is required before condensation begins. Etching techniques were also used by Tweet (45) to give evidence for vacancy clusters in dislocation-free germanium. During the cooling, the crystals become supersaturated with respect to the vacancy concentration and, if no dislocations are present, clusters of vacancies will form. In these crystals the etching rate was much greater than when dislocations were present. Tweet explained these effects in terms of the preferential attack of the acid upon vacancy clusters. Ridges of normal etching rate were found to be connected with spiral dislocations. Normal etching rates were also observed in the neighborhood of the crystal surface, the latter acting presumably as a vacancy sink. Kimura et al. (46) discussed work on quenched-in vacancies in noble metals. They calculated the different decay laws expected for the annihilation of quenched-in vacancies at two types of vacancy sinks, i.e., stray or network dislocations and sessile rings formed by the condensation of vacancies. For quenching from above a critical temperature, it is concluded that most of the vacancies disappear at the sessile rings as divacancies; for quenching from below the critical temperature, most of the vacancies disappear at stray dislocations or network dislocations as single vacancies. They applied their model to the quench-hardening of copper and gold. For high temperatures the hardening is considered to be caused by the formation of sessile rings; for low quenching temperatures by the annihilation of vacancies at pre-existing dislocations. Wilsdorf & Kuhlman-Wilsdorf (47) investigated transmission electron micrographs of quenched aluminum. Instead of the familiar smooth dislocation lines, intricate tangles of kinked and

branched dislocations with interdispersed loops appeared. Vacancy aggregates of up to a few hundred vacancies are believed to exist in these quenched films, and dislocations would be held up when and where their cores meet an aggregate.

Evidence for the existence and the movement of vacancies in ionic crystals is given by the work of Amelinckx *et al.* (48), through the investigation of the cavity formation in nitrate-doped alkali halides. After the annealing of these crystals in a hydrogen atmosphere, cavities were observed along dislocation lines. At the same time, infrared measurements on the crystal showed that the nitrite and nitrate groups had disappeared. It was concluded that oxygen and nitrogen are the gaseous products filling the cavity. Gas in these cavities may be under high pressure and as a consequence will attract vacancies, which will allow the cavities to expand to release the pressure. The growth of a cavity centered on a dislocation probably takes place according to a mechanism similar to that considered by Frank for the growth of a dislocated crystal. Equations for the thermal equilibrium concentration of Schottky vacancies and vacancy pairs in ionic crystals are given by Lidiard (49). The effects due to Debye-Hueckel screening are taken into account in these calculations.

Color centers.—During the past year, fortunately, the number of absorption centers in the alkali halides has not increased substantially. The major emphasis was on the understanding of the physical nature of various defects and the kinetics of their formation. The various color centers in alkali halides are identified and discussed by Seitz (52).

Electron spin resonance studies have provided detailed information about two centers. The first center, studied by Kaenzig & Woodruff (50), is the H-center, which can be described as a halogen-molecule-ion in a halide vacancy. The unpaired electron interacts strongly with the two nuclei of the molecule ion and weakly with two more halogen nuclei. All four nuclei lie in a straight row along a [110] axis. It is interesting to note that the well understood F-center (electron in halide vacancy) and the H-center are complementary centers, i.e., a region of undamaged crystal is restored if an H-center and an F-center are brought together. The second center, investigated by Kaenzig & Cohen (51), consists of a diatomic molecule ion O_2^- which substitutes for a halide ion. Both centers involve interstitial atoms in the alkali halides; the H-center is equivalent to an interstitial halogen atom.

The model of the M-center tentatively proposed by Seitz (52) consists of one electron trapped at a complex of two adjacent negative ion vacancies and a positive ion vacancy. This center has a permanent dipole moment and does not have inversion symmetry. According to the calculations by Overhauser & Ruechardt (53) a large differential Stark effect as measured by line broadening at high external electric fields would be expected. No such effect could be observed on the M-center at applied fields of 3×10^5 v./cm. It was concluded that the M-center has inversion symmetry. Knox (54) modified the original model of the M-center and suggested that a neighboring alkali ion (by jump-

ing into the positive ion vacancy) spends most of its time in the central position between the two negative ion vacancies. Such a configuration has the required inversion symmetry.

During recent years an increasing amount of information has been accumulated on the influence of impurities on the kinetics and interaction of various centers in the alkali halides. The hydroxyl ion, which was first observed by its infrared absorption band, has received special attention. Etzel & Patterson (55) have related an ultraviolet absorption band in NaCl, KCl, and KBr to this impurity. The large differences in the rates of formation of F-centers using x-rays, electrons, and gamma rays are believed to result from the varying OH^- concentration in the crystal (56). Barium ions in the crystal were shown by Shimizu (57) to accelerate thermal bleaching of F-centers and disturb the formation of colloidal centers. Hersch (58) observed an electron surplus center (T-band) when F-centers were bleached in KI crystals containing Tl impurities. The photochemical reaction $F \rightarrow M$ was investigated by Hirai (59) in an additively colored KCl crystal as a function of the F-center concentration. The conversion from F-centers into M-centers appears to go through intermediate states and depends upon the F-center content. In those crystals where the F-centers were produced from U-centers (and as a result H_2 molecules were in interstitial sites) the formation of M-centers was considerably smaller. It is believed that the electrons released from the F-centers during bleaching are captured by the H_2 molecules before being trapped by an M-center. Tomiki (60) also studied the transition $F \rightarrow M$ during optical bleaching and observed the simultaneous creation of A-, R-, and M-centers. By careful heating, the thermally unstable centers could be decomposed leaving only F- and M-centers. It was shown that two F-centers are required to form one M-center. In order to explain quantitative investigations of the transition $M \rightarrow F$, Tomiki (61) had to assume a second absorption band of the M-center hidden in the F-band. The existence of such a band was first deduced by van Dooren (62) from the optical anisotropy of color centers in alkali halides.

For the formation of F-centers, negative ion vacancies have to be created in the alkali halides. Hesketh (63) concluded, from his work on the formation and destruction of F-centers, that vacancies are created by the evaporation from dislocation-jogs of incipient ion vacancies that have trapped electrons. Fischer (64) bombarded single crystals and condensed films of LiF, NaF, and NaCl with 5 kv. electrons at 90°K. The formation of F-centers was measured as a function of the absorbed electron energy up to a saturation value of 10^{20} F-centers/cm.³. The kinetics were strongly influenced by the condensation temperature of the films because of the limited supply of vacancies. Ueta et al. (65) studied the interaction of F- and U-centers under the influence of ultraviolet light in the region of the fundamental absorption. It is inferred from their data that one exciton can bleach at least six F-centers in KCl crystals and one exciton is able to transform three U-centers into F-centers. The investigation of the nature of the V-centers in KBr by Nakai

(66) confirmed the model suggested by Seitz (52) that these absorption bands are produced as a result of the combination of positive ion vacancies. The KBr crystals were additively colored in Br_2 vapor at high pressures, and V-center concentrations ten times higher than observed in earlier experiments were obtained. The electrolytic action of a field on the V-center was also investigated. Similarly, Dunstan (67) colored KBr from point and flat electrodes and formed F- and V-centers. Field emission of excited F-centers was investigated by Luetz (68).

Dislocations.—In recent years, a number of widely varying techniques have been discovered that allow the isolation and study of individual dislocations; the best developed methods are x-ray diffraction, electron microscopy, decoration, and etch pits. With these tools, it is now possible to study directly the mechanism of dislocation formation and the effects of dislocations on other physical properties.

The x-ray technique for the study of individual dislocations was discovered independently by several workers and the methods vary accordingly (69 to 74). Transmission or reflection photographs are taken of an x-ray beam, which is Bragg-reflected from the crystal. The dislocations are revealed by the fact that the intensity diffracted from the neighborhood of the dislocations is different from that of the rest of the crystal. The main advantage of this technique is the nondestructive observation of dislocations in the bulk of crystals. The investigations are mainly concerned with the lighter elements, since the increasing x-ray absorption for high atomic numbers necessitates sample thicknesses in transmission work that are inconveniently small. Bonse (75) found good agreement between the x-ray photographs and theoretical considerations of the effect of the strain fields around dislocations in Ge. Frank & Lang (76) examined dislocations in diamonds and confirmed the idea of Frank *et al.* (77) that most trigons on natural octahedral faces of diamonds are etch pits, which are centered on dislocations. Lang & Meyrick (78) studied the dislocation structures in high-purity recrystallized aluminum, observing a number of kinds of structural features.

Individual dislocations can also be seen by transmission electron microscopy, using sheets of 1000 A or less. The intensity of the Bragg-diffracted electron beam is different in the neighborhood of the dislocation from that in the rest of the specimen. Pashley (79) developed an evaporation technique that allowed him to make thin ($\sim$200 A), detached, single-crystal films of gold, which showed dislocation densities of 10^{10} to 10^{11}/cm.^{2}. Robinson (80) used the electron microscopy technique to investigate dislocation sites along grain fragments in cold-worked aluminum. Thomas *et al.* (81, 82) observed helical dislocations in a transmission electron microscope in quenched aluminum containing 4 per cent copper. It is thought that these helices are produced by the condensation of vacancies on dislocations of predominant screw character.

The detection of dislocations by etching is the oldest and most frequently used technique. However, care has to be taken to insure that the etching re-

agent attacks only dislocation sites and that all dislocations meeting the surface are revealed. Lovell *et al.* investigated dislocations in tellurium (83), bismuth (84), copper (85), and apatite (86) by various etching techniques and showed by deformation-annealing studies and by the analysis of intersecting tilt boundaries that the observed etch pits correspond to dislocations in the specimen. Moran (87) reported various etching solutions for alkali halides.

In recent years the understanding of the mechanism of dislocation formation has increased considerably. After the observation of a Frank-Read source in silicon by Dash (88), it was thought that the main source for dislocations was found. In a series of excellent investigations on LiF, Gilman *et al.* (89) developed an etching technique that allowed them to investigate in detail the formation of dislocations. LiF crystals were subjected to short mechanical pulses (1 to 10 μsec. in length) in order to study the dislocation nucleation. It was found that several heterogeneities can lead to dislocation nucleation, including cleavage steps, dislocation loops, glide bands, inclusions, precipitates (as grown), and radiation-induced precipitates. Gilman concluded that small foreign heterogeneities cause most of the dislocations in real crystals, and that little dislocation multiplication results from the classical Frank-Read source. Most of the dislocation multiplications occur if a prior dislocation moves through the crystal. The generation of prismatic dislocation loops in silicon crystals was investigated by Dash (90), who decorated the dislocations with copper and photographed them with infrared sensitive plates. It was shown that the loops climb as condensation of vacancies continues. Dash further showed that he was able to grow silicon crystals free of dislocations. Wagner (91), studying the growth of germanium, found that most of the dislocations do not originate during growth (Czochralski technique), but result from fast cooling (thermal shock). Washburn & Nadeau (92) studied the dislocation network in a grown LiF crystal by etch pit and decoration techniques, and also found the importance of thermal shock in dislocation formation.

Using their etching technique, Johnston & Gilman (93) measured the velocity of individual dislocations (ranging from 10^{-7} to 10^5 cm./sec.). The growth of total dislocation density and of individual glide bands, and the distribution of glide dislocations during plastic deformation of LiF, were also described by these authors.

The detection of dislocations in α-brass by low-temperature heat conductivity measurements was the subject of a paper by Lomer & Rosenberg (94). The conductivity was reduced by the increased scattering of the phonons by dislocations produced during deformation. The effect on the thermal conductivity of LiF of dislocations introduced by compression was studied by Sproull *et al.* (95) in the temperature range 2–100°K. Below 30°K. the thermal conductivity was approximately proportional to T^2 in agreement with Klemens' theory (96); but the reduction in conductivity by the introduction of dislocations was much larger than Klemens' prediction. Car-

ruthers (97) discussed these results in terms of an enhancement in phonon scattering due to the alignment of dislocations in slip planes during the deformation. He pointed out that reduction in thermal conductivity caused by quenching was considerably less than in the compressed samples, even though the densities of dislocation are comparable. It is thought that the dislocations introduced by quenching were in the form of dislocation loops, but mechanical deformation produced slip planes of thousands of dislocations.

RADIATION DAMAGE

The irradiation of solids by high-energy particles commonly produces damage to the crystal lattice, because the atoms are displaced from their normal sites. Various defects are produced and may be subject to change or annihilation by subsequent annealing of the sample. The study of the production and behavior of such defects—often these are simple vacancies and interstitials—is, of course, closely related to other studies of crystal defects as discussed in preceding sections.

Several aspects of radiation damage in inorganic crystalline solids have been the object of study: (a) the primary mechanism of the damage by the incoming electron, neutron, deuteron, gamma-ray, or other radiation, (b) the identification, structure, and annealing behavior of the defects produced, and (c) the effect of these defects on macroscopic properties of the material, such as mechanical strength, electrical behavior, chemical composition, etc. All of these topics were discussed at length in a conference on radiation damage held in Gatlinburg, Tennessee in May 1959. The papers given at this conference have been published in the August 1959 issue of *Journal of Applied Physics*, to which the interested reader is referred. A review of the general field was given at the conference by Brooks (98).

A good review of the effects of irradiation upon metals has also been given by Seitz (99), who discusses in particular the work that has been done on copper, perhaps the best understood of the metals. Corbett and his co-workers (100, 101) have studied in detail the anealing of copper irradiated by 1.4 Mev electrons, by measurements of the electrical resistivity. At least five substages of the recovery were observed between 14–65°K. The three lowest temperature stages had the characteristics of close-pair recovery, and an attempt was made to correlate these with specific vacancy-interstitial configurations. The remaining two substages represent recovery due to the free diffusion of a defect, presumably interstitial copper; one corresponds to correlated recovery, the interstitial returning to its own vacancy, and the other to uncorrelated vacancy-interstitial annihilation. Evidence was found for trapping of interstitials and for cluster formation, as well as for simple annihilation. It was found also that the populations of the five substages could be shifted by changes in the bombardment energy, the populations of the first three stages increasing at the expense of the last two with decreasing energy. Lattice vacancies in copper are apparently generated with less energy under equilibrium conditions than are interstitials, but the activation energy for

their motion is greater, ~0.75 ev (99). Blewitt *et al.* (102) attempted to measure the stored energy in neutron-irradiated Cu from the rate of warmup with gamma-ray heating. The release of stored energy appears as a reduction in C_P, and in this case occurred in the 30–50°K. range, presumably due to vacancy-interstitial annihilation. From the magnitude of the energy released, it was calculated that the formation energy of a vacancy-interstitial pair must exceed 3 ev.

The irradiation and annealing of germanium has been the subject of much study. Gobeli (103) studied the thermal recovery of electrical properties after α-particle bombardment at 4.2°K., finding a first-order recovery process at around 33°K., which showed an activation energy of 0.02 ev, perhaps representing the recombination of nearby vacancies and interstitials, and also a second stage at around 67°K. MacKay *et al.* (104, 105) and Brown *et al.* (106) have investigated the behavior of electron irradiated germanium. The annealing is complex and is different for n- and p-type material due to differences in the charge state of the defects. None of the observed recovery stages can yet be interpreted with certainty in terms of the simple behavior of a vacancy or interstitial. Lattice parameter changes of germanium irradiated with 9 Mev deuterons have been studied by Simmons (107) and by Balluffi & Vook (108). An interesting effect, emphasizing the long range migrational properties of defects, has been observed in Si using electron spin resonance (109, 110). At room temperature, the dominant defect formed with electron bombardment is composed of a vacancy in a lattice site adjacent to an interstial oxygen atom. Oxygen, known to be present in "pulled" crystals, cannot have migrated to form this complex. In floating zone crystals, with reduced oxygen contents, a complex including phosphorus donors and vacancies was found.

The effects of irradiation on the mechanical or other properties of synthetic sapphire (111), lithium fluoride (112), diamond (113), cadmium sulfide (114), ice (115), solid hydrogen (115), sodium chloride (116 to 118), and simple organic solids (119), as well as a number of metals and alloys, have been studied. Susin & Brinkman (120) made an extensive study of electron-irradiated nickel. Other irradiation studies have been carried out on Ni (121), AuCu (122), Nb (123), Cu (124), Al (125), and Al-Cu alloys (126 to 128).

Thompson (129), using proton irradiation, has observed the interesting "focused collision" effect proposed by Silsbee (130); he observed the preferential ejection of atoms from gold crystals along close packed directions, where a billiard ball effect produces atom displacements over 100 A or more. Leibfried (131) has investigated theoretically the influence of correlated collisions of this type for the *fcc* lattice, comparing the expected range for displacements with the experimental data obtained in copper. Other theoretical treatments of the interaction of radiation with solids include those of Nozieres & Pines (132) for electrons, and Galavanov (133) for x-rays.

Of interest to chemists are the chemical reactions that may result from

the irradiation of a material. One class of these is the so-called "hot-atom" reaction, and Harbottle & Sutin (134) have proposed a model for the chemical effects of nuclear recoil in solids. This model considers the displacement spikes, which constitute local hot spots in the crystal, that are produced in the slowing down of energetic atoms. These hot spots merge to give a relatively uniform zone of high temperature, which has a lifetime of $\sim 10^{-11}$ sec., during which chemical reactions involving the recoil atom may occur. Milman (135) has studied the Szilard-Chalmers effect in solid ethyl bromide, and the radiation decomposition of crystalline $KBrO_3$ has been investigated by Boyd & Cobble (136). A different type of chemical reaction produced by irradiation was studied by Moore (137) who investigated the dissociation of solid SrO by the impact of slow electrons. Proton irradiation was shown by Simnad et al. (138) to influence strongly the hydrogen reduction of NiO. The initial induction period was shortened because of the formation of new nucleation sites, and the subsequent reduction was accelerated because of the enhancement of diffusion-controlled processes by the additional defects produced in the bombardment.

Solid State Reactions

The work to be mentioned in this section may be classified as: (a) studies of heterogeneous reactions (reactions involving the transport of atoms or ions across a solid-solid interface), (b) studies of homogeneous reactions (reactions involving the rearrangement of atoms or ions within a solid solution), and (c) studies of nucleation and nuclei growth (reactions initiated with a solid solution that lead to a heterogeneous reaction). It is the kinetics of these reactions that are of chief interest.

Heterogeneous reactions.—Corrosion reactions, which produce a layer of a solid phase (or phases), usually of an oxide, on the surface of a metal or semiconductor, have received major attention. Such reactions may occur with or without an applied field. The reactions that occur at a metallic anode to give films through which reacting species must migrate in order for the film to grow have been discussed by Hoar (139) in an excellent review article which is a general discussion of the anodic behavior of metals. The reader is referred to this article for an up-to-date account of theory and experiment.

The rate of oxidation is usually determined either by transport processes through the growing layer or by transport processes across or in the region of the solid-solid interface (in some cases both processes may be important; it is also possible that the rate limitation may occur at the surface layer—ambient interface). When the rate limitation is the rate of charge carrier movement within the solid layer, the rate law is frequently parabolic ($d^2 = kt + c$; where d is layer thickness, t is time; and k and c are constants that are functions of temperature and of the pressure or concentration of components in the ambient). A theory proposed by Wagner (140), which accounts for the growth rate in terms of transport processes through the layer, is usually used to account for the magnitude of k. When the films are very thin, an electric field

may penetrate the surface layer and influence the transport processes. This effect has been accounted for in a theory [proposed by Mott & Cabrera (141)] leading to rate laws that range from linear, through parabolic and cubic, to logarithmic, depending upon the layer thickness and film conductivity type. Modifications of these theories have been proposed from time to time to account for the oxidation rates in more complex systems.

The anodic oxidation of tantalum is a process of considerable practical and theoretical interest. It has been established that ion migration is the rate-limiting process in the growth of these films, but the species responsible has not been established. Verkerk *et al.* (142) have used radioactive tantalum to study this process and have concluded that tantalum is the migrating species, but the mechanism of movement is neither a pure vacancy mechanism nor a pure interstitial process. Young (143) has found that the anodic oxidation of zirconium differs markedly from that of tantalum and niobium. He has concluded that the ion movement is controlled both by the interface barrier and the diffusion barrier within the film, in keeping with a model originally proposed by Haring (144) and put on a quantitative basis by Dewald (145).

Hoar & Mott (146) have concluded from their studies of the formation of porous anodic oxide films on Al that both oxygen and aluminum must be capable of diffusing through the compact part of the film. They suggest that OH^- is the diffusing species responsible for the movement of oxygen since it seems unlikely that the large O^- ions will migrate.

A general rate equation that accounts for the transition from parabolic to linear kinetics during metal scaling has been derived by Haycock (147). A secondary process such as scale recrystallization is assumed to act to maintain a barrier scale of constant thickness, which was first formed by a diffusion process giving a parabolic growth. Wallwork & Jenkins (148) have studied the high temperature oxidation of titanium, zirconium, and hafnium and find that a transition from parabolic to linear rate laws occurs; they explain this in terms of a constant oxygen gradient into the metal from the oxide interface. The transition from parabolic to linear behavior occurs when the metal becomes saturated with oxygen at the interface. The measurements of Mallett *et al.* (149) on the diffusion and solid solubility of oxygen in zirconium seem to be in accord with the work of Wallwork and Jenkins.

The change in conductivity of anodic zirconium oxide films upon heating in vacuum was attributed by Misch & Gunzel (150) to the diffusion of anion vacancies into the oxide. The increased oxide growth rates were believed to corroborate this conclusion.

Uhlig *et al.* (151) conclude that the initial oxidation rates of nickel can be represented by a two-stage process, both of which are logarithmic, the first faster than the second. In addition, they find a discontinuity in the rate at the Curie temperature; they ascribe this discontinuity to a change in work function of nickel on the assumption that electron transfer from metal to oxide is the rate-limiting step. Smetzer (152) has studied Ni-Co alloys in the range of the Curie temperature and has used cubic and parabolic equations

to fit the data. He also finds a discontinuity in the rates at the Curie temperature.

The effects of the stresses in the Cu_2O layer in the oxidation rates of copper have been discussed (153). The outward diffusion of Cu^+ ions through the Cu_2O layer is believed to be the rate-limiting step, but at lower temperatures whisker extrusion is taken as evidence that extra vacancies are being generated. When the temperature is high enough the film can plastically deform and only thermal vacancies are present. This permits an explanation of the higher activation energy for oxide growth at the higher temperature. Meijering & Verheijke (154) conclude that the cubic oxidation relation found for Cu_2O can be explained in terms of aging effects in the CuO layer.

Haycock (155) has proposed a mechanism for the high temperature sulfiding of iron which requires a proton to be trapped at metal-ion vacancies in the sulfide barrier layer.

Homogeneous reactions.—Reiss (156) has written a review paper on diffusion-controlled reactions in solids, examples of which are the annealing of radiation damage, ion pairing, and the formation of complexes in solids, as well as precipitation reactions in semiconductors.

Review articles by Fuller (1, 157) describe studies that have been made of interactions that occur between solutes in Ge and Si. These include the interactions of several of the group III acceptors with oxygen in silicon as well as the interactions of lithium with oxygen in silicon.

Kaiser *et al.* (158) have been able to account for the complex annealing kinetics of oxygen-doped silicon in terms of the formation of donor states in silicon arising from aggregates of two, three, and four oxygen atoms. The configuration of four oxygen atoms around one silicon atom appears to be the most important electrically.

Evidence for the association of oxygen atoms in interstitial solid solutions in tantalum has been presented by Powers & Doyle (159).

Nucleation and precipitation.—Tweet (160) has reviewed the status of precipitation phenomena in semiconductors, pointing out that the evidence for metastable centers in the precipitation of Li in Si and of SiO_2 in Si emphasizes the need of a consistent nucleation theory that will account for the relatively long lifetime of centers containing only a few atoms.

Ham (161) has re-examined the theory of Cottrell & Bilby (162) for stress-assisted precipitation on dislocations. He finds that the $t^{2/3}$ law for the fraction precipitated is not correct over the range of time during which most of the precipitation occurs and concludes that the mechanism of precipitation of carbon in β-Fe is not yet clearly established. Ham (163) has also derived growth law for the diffusion-limited growth of particles that are disks and rods. The growth law t^n has an exponent of 2 for disks of constant thickness in the approximation for short times. Rods of constant radius have $n = 1$ and both disks and rods of constant ratio for their long to short dimensions have $n = 3/2$.

The kinetics of cellular segregation reactions such as discontinuous precipitation and pearlite formation have been discussed by Cahn (164).

Boltax (165) has suggested that vacancy clusters may grow during the quenching of a solid and form sessile rings, which may act as nucleation centers for precipitation. Amelinckx (166) presents evidence that x-ray irradiation may also produce nucleation centers for precipitation in the alkali halides, which may be small prismatic dislocation loops resulting from vacancy condensation.

An experimental test of the Volmer theory of homogeneous nucleation, in which the contact angle of the condensate in a surface determines the critical supersaturation ratio, has been tested and confirmed by Twomey (167). Fletcher (168) has discussed the effect of dipole orienting substrates in the entropy of adsorbed water molecules and the influence this has upon the nucleation of ice crystals.

The precipitation of indium oxide in zinc oxide has been studied by Thomas (169); he was able to explain the rate of change of electrical conductivity in terms of precipitation along lines, believed to be dislocations, at a density of 10^7 cm^{-2}.

CRYSTAL GROWTH

An international conference on crystal growth was held on August 27–29, 1958, in Cooperstown, N. Y. The proceedings of this conference have been published under the editorship of Doremus, Roberts & Turnbull (170). A number of excellent review articles are included among the numerous significant papers presented at the conference (170): Nabarro & Jackson have reviewed the work on "Growth of Crystal Whiskers," Brenner on the "Properties of Whiskers," Chalmers on the "Growth of Crystals of Pure Materials and of the Solvents of Solutions," Mandelkern on the "Crystallization Kinetics in Polymer Systems," and Keller on the "Morphology of Crystalline Polymers," while Cabrera & Vermilyea discuss the "Growth of Crystals from Solution" and present a theory of growth in terms of the flow of steps across the surface of a crystal and the bunching of these steps. A similar point of view was used by Frank in a paper entitled "On the Kinematic Theory of Crystal Growth and Dissolution Processes" (170). There are 34 additional papers in this important volume on the fields covered in the review papers, plus an introductory lecture by Frank, and numerous "Discussion" sections.

During the past year, a large number of papers have appeared that describe the growth of single crystals of a variety of solids. Several extensive review articles on single-crystal growth methods have appeared. Tanenbaum (1, 171) has emphasized semiconductor crystal growth while Honeycombe (172) has discussed the growth of metal single crystals. The control of impurities during crystal growth from the liquid phase was discussed by Thurmond (1).

The production of dislocations and their elimination during crystal growing from the melt were discussed in an earlier section (89 to 91, 170). The effects that crystal rotation has on the oxygen content of Si crystals pulled from SiO$_2$ crucibles have been studied by Goss & Adlington (173).

Single crystals of bismuth have been pulled from the melt by Porbansky (174). Carlson (175) has made single-crystal tungsten rods by zone refining, using electron bombardment to supply heating energy. Strain anneal and the Bridgman method have been used to grow single crystals of stainless steel (176).

The growth of crystals of various III–V compounds has been reported [GaP (177), GaAs (177, 178), InP (177, 179), InAs (177, 180), InAs-GaAs solid solutions (181), and InSb (182)]. Small crystals of GaP, GaAs, InP, and InAs were made by vapor-phase gas reactions as reported by Antell & Effer (177). Whiskers of InAs were obtained.

Sulfides, selenides, and tellurides of zinc, cadmium, and mercury have been prepared as single crystals and their properties discussed [ZnS (183 to 185), CdS (183 to 188), ZnSe (185), CdS-CdSe solid solutions (189), HgTe (190, 191), and HgTe-CdTe solid solutions (190)]. Two new methods of forming crystallites of SiC have been reported by Smith (192) and by Merz & Adamsky (193). The latter workers have synthesized the wurzite form of SiC.

The noncubic semiconductor Cd_3As_2 was prepared by Rosenberg & Harman (194), and found to have a surprisingly high mobility (10,000 cm.^{2}/volt sec.).

Several interesting papers on oxide crystal growth have been reported. Lynch & Lander (195) have grown single crystals of BaO, and Claussen & MacKenzie (196) have been able to crystallize B_2O_3 at high pressures. Laudise (170, 197) has discussed the kinetics of hydrothermal quartz crystallization while Barrer et al. (198) have described the conditions for low-temperature hydrothermal crystal growth of aluminosilicates and some gallium and germanium analogues.

The effects of poisons in crystal growth have been discussed by Sears (170, 199). Fleischer & Davis (200) have devised a method of controlling the position of grain boundaries in bicrystals grown from the melt. Solid phase crystal growth, or, as it is usually called, grain growth or recrystallization, has been studied by Holmes & Winegard (201 to 203) in tin and lead. They have concluded that grain boundary migration during normal grain growth, and grain boundary self-diffusion and liquid self-diffusion proceed by the same elementary process. Vandermeer & Gordon (204) have studied recrystallization in zone-refined Al and find evidence for edge-nucleated, growth-controlled recrystallization. Blade et al. (205) have shown that the recrystallization temperature of cold-worked aluminum can be lowered to around 100°C. by continued zone refining.

Thin films.—The proceedings of an international conference on the structure and properties of thin films were published at the end of the year (205a). This volume contains some forty papers dealing with the formation of thin films and their mechanical, electrical, and magnetic properties. A section on chemical interactions at surfaces is included. Bassett & Pashley (206) have written a comprehensive paper on the growth, structure, and mechanical properties of their films. Vermout & Dekeyser (207) attempted an interesting

but difficult experiment and met with partial success. They found that evaporated silver films on carbon replicas of a cleaved NaCl crystal substrate were oriented. The films deposited in the opposite cleaved face were single crystal. They point out that this means that the geometry of the substrate, as well as lattice matching, plays an important role in the orientation of the film. The effect of substrate crystalline imperfections in epitaxial growth of Fe_3O_4 crystals on silver crystals has been studied by Chatterji (208). Crystal growth in sputtered copper films has been studied by Henschke (209).

Whiskers.—There has been some question about the effect of thin oxide films upon the mechanical strength of whiskers. Brenner (170) suggested that Au whiskers should be tested since there should be no oxide coating present. The experiment was subsequently performed by him (210). He concluded that surface films probably are unimportant since the strength of the gold whiskers was the same as copper and tin whiskers. Webb & Stein (211) found that copper and silver whiskers maintained their strength even after extensive efforts had been made to remove surface films.

Ellis, Gibbons & Treuting (170) have shown that whisker growth on a metal substrate by base growth can be explained as a recrystallization process with mass transfer. The grain boundary of the nucleating crystallite is believed to be anchored; if this occurs, the free energy is decreased by the growth of whiskers rather than grains. A dislocation mechanism of whisker growth may be operative in some systems.

Morelock & Sears (212) and Brenner (213) find that copper whiskers are grown at low supersaturation by the hydrogen reduction of CuI, which is adsorbed on the tip of the whisker. Brenner finds that this occurs below the melting point of CuI. Above the melting point the rate of growth goes up rather abruptly. Allan & Webb (214) have found that a copper whisker grown by the hydrogen reduction of CuCl grows from both the base and the top. They find no evidence of axial dislocations in their whiskers. Gorsuch (215) finds no evidence of elastic twist (Eshelby twists) in Fe whiskers grown by hydrogen reduction of iron halide salts. Sears (216) has found evidence of elastic twists in LiF whiskers grown from aqueous solutions. The growth of Al_2O_3 whiskers has been studied by DeVries & Sears (217), who were able to follow the growth of these whiskers at high temperature under a stereomicroscope. The screw dislocation theory of crystal growth accounts for the general behavior of these whiskers. Sears (218) has proposed a growth mechanism for the scroll habit of graphite whiskers. Wiedersich (219) has studied the growth forms of silicon crystals formed by zinc reduction of $SiCl_4$ and iron crystals formed by the hydrogen reduction of $FeCl_2$. The dependence of the growth forms on the partial pressure of the reacting components in the gas (ranging from equiaxed crystal to whiskers) leads to the conclusion that the adsorption of components on different crystallographic planes rendered some faces inactive to further growth.

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SOLUTIONS OF NONELECTROLYTES[1]

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A most significant contribution to the field of solutions this year was Debye's (1) treatment of light scattering and critical opalescence in liquid mixtures. The range of measurement has been extended to the sizes of ordinary molecules.

Rowlinson's book, entitled *Liquids and Liquid Mixtures* (2) which was published this year, contains an abundance of well organized information not found in other reference books. It is well documented with material from the recent literature; some of it as late as the middle of 1958. The first two volumes of Timmermans' *The Physico-Chemical Constants of Binary Systems in Concentrated Solution* (3) were published and represent a compilation of all the existing data on binary systems in tabular form. It is regrettable that complete bibliographic references were not included in each volume.

Each year, a larger group of investigators, interested in the thermodynamic properties of solutions, express their results in terms of the power series expansion, $y = x_1 x_2 [a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2 \cdots]$, suggested by Guggenheim (4). Applications and advantages of its use have been discussed by Redlich & Kister (5) and by Scatchard (6). Whether or not this is the best form is not argued here. That a large number of workers desire to express their results in the same form represents significant advancement.

Gas Mixtures

The second virial coefficient of a mixture of two gases may be represented by the relationship:

$$B_M = (1 - x)^2 B_{11} + 2x(1 - x)B_{12} + x^2 B_{22} \qquad 1.$$

where x is the mole fraction of the component 2. B_{11} and B_{22} are the second virial coefficients of the pure components and B_{12} represents the 1-2 interactions. For mixtures that follow the same law of corresponding states, the following combining rules of Guggenheim & McGlashan (7) obtain:

$$\frac{B_{12}}{V_{12}^*} = f\left(\frac{T}{T_{12}^*}\right) \qquad 2.$$

where

$$T_{12}^* = (T_{11}^* T_{22}^*)^{1/2} \qquad 3.$$

and

$$V_{12}^* = \tfrac{1}{8}(V_{11}^{*1/3} + V_{22}^{*1/3})^3 \qquad 4.$$

T_{11}^*, T_{22}^*, V_{11}^*, V_{22}^* are the critical temperatures and critical volumes of the pure components, and f is a function common to both. Measurement of the temperature dependence of second virial coefficients of pure and mixed gases established the function f, and serves as a test of the various combining rules.

Garner & McCoubrey (8) measured the second virial coefficients of n-pentane, perfluoro-n-pentane, perfluoro-n-hexane, and binary mixtures of n-pentane with the two fluorocarbons over a 75 degree temperature range and at several compositions. These are the first such data for mixtures of fluorocarbon and hydrocarbon vapors. Plots of B/V^* against T/T^* for the three pure substances were smooth curves, but deviated considerably from the curve suitable for substances obeying the Lennard-Jones 12-6 potential for spherical molecules, the order of the deviations being: perfluoro-n-hexane > perfluoro-n-pentane > n-pentane. The second virial coefficients for perfluoro-n-pentane are larger (numerically) than those for the corresponding hydrocarbon. Since the three substances did not obey the same law of corresponding states, these investigators compared their experimental values of B_{12} with those obtained from a graphical average of the corresponding-states plots assuming B_{12}/V_{12}^* to fall midway between the curves for the two pure components, and then calculated B_{12} from Equations 3 and 4. The calculated values of B_{12} are approximately 20 per cent larger (numerically) than the experimental values, indicative of rather weak 1-2 cohesive forces. This author has calculated the force constants from the 12-6 potential and finds $\epsilon_{12} = 0.92$ $(\epsilon_{11}\epsilon_{22})^{1/2}$ for the pentanes system and $\epsilon_{12} = 0.95$ $(\epsilon_{11}\epsilon_{22})^{1/2}$ for the other. In liquid mixtures of fluorocarbons and hydrocarbons a corresponding factor of 0.94 applied to the geometric mean approximation would correlate all of the data rather well.

Prausnitz (9) has modified Equation 3 to

$$T_{12}^* \cong k_{12}(T_{11}^* T_{22}^*)^{1/2},$$

where

$$k_{12} \sim \left(\frac{4\beta}{(1+\beta)^2}\right)\left(\frac{2\zeta^{1/2}}{1+\zeta}\right) \qquad 5.$$

and

$$\beta = \frac{V_{11}^*}{V_{22}^*}, \qquad \zeta = \frac{I_2}{I_1}$$

as derived from London dispersion force theory, where I's are the ionization potentials of the molecules. (Actually only the attractive branch of the interaction potential is considered here.) When Reed's (10) estimates of the ionization potentials are used, we find $k_{12} = 0.93$ for the above pentane-fluorocarbon systems. Prausnitz (9) has also computed values for the generalized function f' in the relationship

$$\frac{C_{ijk}}{(V_{ijk}^*)^2} = f'\left(\frac{T}{T_{ijk}^*}, (\omega_{ijk})\right)$$

based on Pitzer's (11) generalized compressibility tables and on volumetric data for argon, nitrogen, methane, n-butane, and n-heptane.

Lambert and co-workers (12) determined the second virial coefficients of binary mixtures of chloroform with methyl formate, n-propyl formate, methyl acetate, ethyl acetate, and diethylamine between 50 and 95°C. The values obtained are more negative than predicted by corresponding-states theory. Equilibrium constants for the associations and their dependences on temperature were calculated. The derived heats of association with $CHCl_3$ range from -1800 cal. mole^{-1} to -6020 cal. mole^{-1} in the following order: methyl acetate (-1800) >ethylacetate >diethylamine >methyl formate >n-propyl formate >diethyl ether. If hydrogen bonds are formed exclusively through the carbonyl oxygen, the order should correspond to increasing nucleophilicity of the carbonyl oxygen. The authors suggest that the formates bond through the alkoxy oxygen and that the acetates bond through the carbonyl oxygen.

Prausnitz & Bensen (13) have determined the second virial cross coefficients, B_{12} at 15°C. for hydrogen, nitrogen, and carbon dioxide with carbon tetrachloride, iso-octane, toluene, and n-decane from measurements of the solubility of the liquids in the compressed gases as a function of pressure. Equation 9 was used to estimate the activity coefficients of the liquids in the liquid phase where this was important. The second virial cross coefficients were calculated for the 12 binary systems at 50 and 75°C. and are accurate to about 5 cm.^{3}.

Richardson & Rowlinson (14) extended their solubility measurements of mercury in n-butane gas up to 300° C. and 400 atm. From these data, one may calculate B_{12}.

CRITICAL REGION STUDIES

Meeks, Gopal & Rice (15) have examined the effect of water on the critical solution curve of the cyclohexane+aniline system at controlled activity. For previous discussions of the effect of impurities see Rice (16) and Atack & Rice (17). Activity was controlled by equilibrating the mixture with the lithium sulfate+lithium sulfate monohydrate pair, the resulting water concentration being less than 5×10^{-5} mole cm.$^{-3}$. The coexistence curve was raised 0.3°, the increase being greater for the cyclohexane-rich mixtures. The flat portion was practically destroyed.

Schmidt, Jura & Hildebrand (18) have confirmed earlier studies (19) of the behavior of the heat capacity in the critical region. The differences in heat contents between 0°C. and several temperatures slightly above the critical solution temperature were determined for a critical mixture of carbon tetrachloride and perfluoromethylcyclohexane, using a Bunsen ice calorimeter. The ice calorimeter was particularly suited to this experiment because an appreciable equilibration time (at least 60 hr. in the example cited) was required in the region immediately above the separation temperature. The heat capacities were obtained from temperature derivatives of the

heat contents. The λ shaped heat capacity curve extends at least seven degrees above the critical solution temperature.

Reed & Taylor (20) found that the viscosity is a rather sensitive indicator of the nonhomogeneous state, which obtains near and above the critical
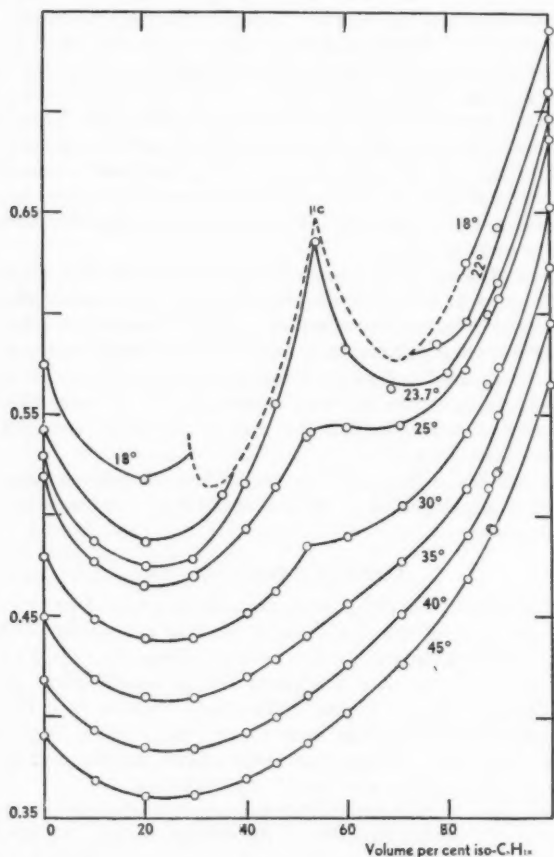
FIG. 1. Viscosity versus composition for iso-C_8H_{18}+n-C_7F_{16} [Reed, T. M., and Taylor, T. E., $J.$ $Phys.$ $Chem.$, **63**, 58, Figure 10 (1959)].

solution temperature. Reed & Taylor's data are shown in Figure 1 for the system: iso-octane+perfluoro-n-heptane, for which the critical solution temperature is 23.7°. The authors have calculated an "excess free energy of activation" from Eyring's absolute viscosity theory. A plot of this excess

function shows an inflection as high as 45°C. above the separation temperature. The viscosities and densities of ten solutions were reported. In connection with viscosity and clustering, the reader's attention is called to a paper by McLaughlin & Ubbelholde (21). They discovered that o-terphenyl has an excess viscosity persisting to some 140° above the melting point, which they interpret as due to clustering.

In a paper on the angular dissymmetry of scattered light in the critical region, Debye (1) has devised a theory relating the dissymmetry to the range of molecular forces for mixtures of ordinary molecules and, in the case of polymer molecules, to sizes too small to be studied by the usual scattering methods. The theory is based on the fact that the compressibility of the fluid becomes very large in the critical region and that the work of compression required to produce a density fluctuation of certain amplitude will be small. Under these circumstances, an additional term, which depends on the average square of the local gradient of the fluctuation, becomes important.

The approach in the paper cited is essentially a thermodynamic one. The free energy of the mixture, relative to the pure components, contains, in addition to the usual terms for the energy and entropy, a term associated with the local fluctuations in composition. The Fourier component, Λ, of the fluctuation in composition is related to the wavelength of the light λ in the medium by $1/\Lambda = s/\lambda$ where $s = 2 \sin(\phi/2)$.

Debye's equation for the Helmholtz free energy of the mixture is then

$$\frac{F}{VkT} = \frac{F^0}{VkT} + \frac{1}{4}\left(\frac{\eta_0}{\phi_2}\right)^2\left[\phi_2\partial/\partial\phi_2(P/kT) + 4\pi^2\phi_2{}^2H/kT\,(s^2/\lambda^2)\right] \qquad 6.$$

where F^0 is the free energy of a homogeneous mixture, ϕ the usual volume fraction, P is osmotic pressure, and η_0 is an amplitude associated with a local fluctuation in volume fraction. H is a term of cohesive energy densities and length, and depends upon a model. The quantity in brackets is associated with the local density gradients, and Debye incorporates the second term as a correction into Einstein's classical light scattering equation as follows:

$$\frac{I}{I_0} = 4\pi^2\,\frac{V}{R^2\lambda^4}\left[\frac{1 + \cos^2\theta}{2}\right]\,\frac{[(c/u)(\partial u/\partial c)]^2}{\phi_2(\partial/\partial\phi_2)(P/kT) + 4\pi^2\phi_2{}^2(H/kT)(s^2/\lambda^2)} \qquad 7.$$

Here I is the intensity of light scattered at angle ϕ, R is the distance from a scattering volume V, u is the refractive index, and c is concentration. The derivative of the osmotic pressure will be recognized as being connected with the change in chemical potential with composition. The critical solution temperature and composition can then be obtained from the model by setting the first and second derivatives of the chemical potential, with respect to composition, equal to zero. The osmotic pressure also can be expressed in terms of the model. When these are introduced into Equation 7, the scattering intensity can be calculated as a function of temperature and angle.

The relationship for the scattered intensity then becomes:

$$\frac{I}{I_0} = \frac{4\pi^2V}{R^2\lambda^4}\left[\frac{1 + \cos^2\theta}{2}\right](1 + \sqrt{V_2/V_1})^2\left(\frac{kT}{\Omega}\right)\,\frac{[(c/u)\partial u/\partial c]^2}{[Tc/T - 1] + 4\pi^2(H/\Omega)(s^2/\lambda^2)} \qquad 8.$$

where Ω contains cohesive energy-density terms. The ratio H/Ω has the dimensions of length squared. Since both H and Ω are based on the same model, the deficiencies of the model chosen largely cancel. It is easily seen that the dissymmetry of scattered light increases very rapidly as one approaches the critical point. In Debye's model, $H/\Omega = l^2/6$ where l is considered as a range of molecular forces.

The temperature dependence of the angular dissymmetry, which has been calculated by Debye, has been verified experimentally by Zimm (22), who observed for the perfluoromethylcyclohexane+carbon tetrachloride system that, although opalescence persisted several degrees above the critical solution temperature, the variation of intensity with angle extended only about one degree above the separation temperature, and then within a range of about 10 volume per cent. Debye has reported that Zimm has recalculated his data and finds that $l = 14.7$ A.

The fluctuations treated by Debye are local composition gradients that increase the free energy (or decrease the entropy) and are not responsible for the large excess heat capacity up to 7° above the critical solution temperature that has been observed by Schmidt, Jura & Hildebrand (18). These are small perturbations on an already existing nonrandom and nonhomogeneous system.

Several other papers treating the thermodynamics of nonuniform systems have appeared this year. The reader is referred to papers by Hart (23), Cahn (24), and Cahn & Hilliard (25, 26).

Liquid Mixtures

Solutions at low temperatures.—Walling & Halsey (27) have studied the argon-krypton system by determining the frost points of gaseous mixtures up to 20 per cent argon at four temperatures between 82.4°K. and 98°K. They find that W_{AB} (i.e., $\bar{F}^E = W_{AB}x_1x_2$) decreases with increasing temperature and is a function of composition. Curiously, W_{AB} decreases with increasing argon concentration at -82.4°K. and is an increasing function at higher temperatures. The limiting value of W_{AB} as $x_{\text{Ar}} = 0$ is given by $W_{AB}^0 = 330 - 1.9\ T \pm 25$ cal. mole^{-1}.

Heastie (28) studied the argon-krypton system over the entire composition range by determining the total pressure of 20 different mixtures over a temperature range that included the melting and freezing points of the mixtures. He deduced the solid-liquid phase diagram from the discontinuities in the slopes of $(\log P, 1/T)$ graphs. W_{AB} was calculated at 82.9° and appears to increase with increasing argon concentrations over the whole range. From Heastie's graph, we estimate $\bar{F}^E$ cal. mole$^{-1} = x(1-x)[190 + 50(1-2x)]$, where x is the mole fraction of krypton. The molar excess free energy at $x = 0.8$ is 160 cal., in agreement with Walling & Halsey, but the overall concentration dependence has the opposite sign. When one carefully examines Heastie's graph between $x = 0.8$ and 0.95 mole fraction krypton, the region studied by Walling & Halsey, Heastie's four points taken by

themselves would corroborate the work of Walling & Halsey. The data are not precise enough to establish a minimum. The slope of W_{AB} vs. x is opposite to that in the system krypton+xenon studied by Freeman & Halsey (29) where W_{AB} is larger for solutions more rich in the larger molecule.

Bellemans (30) has calculated the excess free energies from the boiling point and dew point data of Newman & Jackson (31) for the systems: H_2 +D_2 and H_2+HD at 20°K. The values of $\tilde{F}^E$ cal. mole^{-1} from the boiling point and dew point data for the former systems are given by 6.2 x_1x_2 and 6.8 x_1x_2 respectively. The corresponding values for the latter are 2.6 x_1x_2 and 2.4 x_1x_2.

Knapp (32) has analyzed liquid-vapor equilibrium data for the system methane + nitrogen and finds at $x=\frac{1}{2}$ and 100°K., that $\tilde{H}^E \cong 22$ cal. mole^{-1}.

Streng & Grosse (33) report that carbon monoxide is completely miscible with liquid ozone at 77.4°K. while nitrogen has limited miscibility with ozone. The ozone and nitrogen phases contain 8.8 and 95.5 per cent nitrogen respectively. The system oxygen+ozone is known to have limited miscibility (34). Streng & Kirshenbaum (35) report that liquid oxygen and liquid methane are miscible in all proportions down to 77°K. when solid methane separates. Kirshenbaum & Grosse (36) have investigated qualitatively the solubility properties of ozone fluoride, O_3F_2 ($\delta_{90°K}=6.6$). They find this new substance to be insoluble in fluorine, nitrogen, and oxygen at 77°K., but slightly soluble in oxygen difluoride at 90°K. and completely miscible with it at 116°K. At the latter temperature, it is slightly soluble in carbon tetrafluoride and soluble in dichlorodifluoromethane and trifluorochloromethane.

Din & Goldman (37) have determined the solubility of nitrous oxide in liquid oxygen between 75° and 94°K. The solubilities are considerably less than the ideal value and are about 2.5×10^{-1} moles mole^{-1} at 78°K. and 14.2 $\times 10^{-3}$ moles mole^{-1} at 94°K.

Cosway & Katz (38) have reported liquid-vapor equilibrium data for three ternary systems containing hydrogen, nitrogen, methane, and ethane and the quaternary system at 500 and 1000 p.s.i. and at −200 and −100°F.

Fluorocarbon solutions.—The first reported properties of fluorocarbon solutions were discussed by Hildebrand & Scott (39) in the first *Annual Review of Physical Chemistry*. These solutions were iodine in perfluoro-*n*-heptane (n-C_7F_{16}), and perfluoromethylcyclohexane with benzene, carbon tetrachloride, chlorobenzene, chloroform, and toluene. Their solubilities, critical solution temperatures, and compositions were found to be in excellent agreement with those calculated from the solubility parameter equations:

$$\overline{F}_2{}^E = RT \ln (a_2/x_2) = \tilde{V}_2\phi_1{}^2(\delta_2 - \delta_1)^2 \qquad 9.$$

$$RT_c = \frac{2x_1x_2\tilde{V}_1{}^2\tilde{V}_2{}^2}{(x_1\tilde{V}_1 + X_2\tilde{V}_2)^3} (\delta_2 - \delta_1)^2 \qquad 10.$$

$$X_{tc} = \frac{(\tilde{V}_1{}^2 + \tilde{V}_2{}^2 - \tilde{V}_1\tilde{V}_2)^{1/2} - \tilde{V}_1}{\tilde{V}_2 - \tilde{V}} \qquad 11.$$

of Scatchard (40) and of Hildebrand (41). In these equations T_c and X_c refer to the critical solution temperature and composition, $\bar{V}$'s are molal volumes, $\bar{F}^E$ is the excess partial molar free energy of solution, ϕ the volume fraction, and δ is the solubility parameter defined as the square root of the energy of vaporization per unit volume. Before the review by Hildebrand & Scott (39) was published, studies of solutions of fluorocarbons with aliphatic hydrocarbons (42, 43) demonstrated the failure of the above equations in these cases. In 1958, Scott (44) reviewed the existing data of some 64 systems containing fluorocarbons and judged that the anomalous behavior must be attributed to a failure of the geometric mean law ($\epsilon_{12} = \epsilon_{11}^{1/2}\epsilon_{22}^{1/2}$) rather than to a special entropy or volume effect. In 1959, the virial coefficients of mixtures of fluorocarbon and hydrocarbon vapors were published, and the data supported Scott's conclusion regarding the geometric mean law. Carefully determined calorimetric heats of mixing that help resolve some inconsistencies in the existing thermodynamic data were reported. A theory was proposed by Reed (45) that the polarizabilities of molecules in these mixtures are different from their polarizabilities in the pure substances, accounting in part for the success of Equation 10 for solutions of fluorocarbons with carbon tetrachloride, and for its failure in the case of fluorocarbons with aliphatic hydrocarbons.

Kyle & Reed (46) have determined the mutual solubility diagrams for fourteen systems containing fluorocarbons, twelve of which are new. They also measured the total vapor pressure as a function of temperature over the two-liquid range for six of these systems. The solubility data on the systems $n\text{-}C_7F_{16}+CCl_4$ and $n\text{-}C_7F_{16}+n\text{-}C_7H_{16}$ substantiate the earlier work by Hildebrand, Fisher & Benesi (42). Consolute temperatures and compositions for the new data are shown in Table I, together with those calculated from Equations 10 and 11.

Agreement between the critical solution compositions calculated by means of Equation 11 and experiment adds strength, but does not prove the correctness of the functional form of Equation 9 from which it was derived. Kyle & Reed point out that the solubility in conjugate phases of the systems, $C_7F_{14}+CHCl_3$, $C_7F_{14}+C_6H_6$, and $C_8F_{16}O+C_7H_8$, below the critical solution temperature, are not in accord with Equation 9. Similar disparities in fluorocarbon-hydrocarbon systems were pointed out by Rotariu, Hanrahan & Fruin (47) except that they used the Flory-Huggins partial molal entropy $-R[\ln \phi_2 + \phi_1(1 - V_2/V_1)]$ instead of the ideal value $-R \ln X_2$, in their expression for the excess partial molal free energy. Shinoda & Hildebrand (48) have shown that the ideal entropy term is more satisfactory than the Flory-Huggins relation for calculating critical solution compositions.

If we compare the data of Table I with past experience we discover two new anomalies. The calculated critical solution temperatures for $(C_4F_9)_3N+C_7H_8$ and $CH_3COC_2H_5+C_8F_{16}O$ are as far above the experimental values as those that have incited so much interest in the past are below them. The behavior of 1-hydroperfluoroheptane resembles that of the fluorocarbons in the aromatics, aliphatics, and alicyclic compounds shown.

TABLE I

The Comparison of Calculated and Observed Consolute
Temperatures and Compositions

	Temp., °K.		Composition	
	Obs.	Eq. 10	Obs.	Eq. 11
$C_6H_5CH_3-C_8F_{16}O$	386	377	0.73	0.77
$C_6H_5CH_3-(C_4F_9)_3N$	415	660	.82	.87
$C_6H_5CH_3-C_7F_{15}H$	309	266	.75	.74
$n\text{-}C_7H_{16}-C_8F_{16}O$	320	130	.63	.67
$n\text{-}C_7H_{16}-C_7F_{15}COOCH_3$	306	84	.67	.69
$n\text{-}C_7H_{16}-C_7F_{15}H$	305	99	.61	.63
$n\text{-}C_7H_{16}-(C_4F_9)_3N$	355	286	.79	.78
$C_6H_{11}CH_3-C_8F_{16}O$	338	189	.74	.71
$C_6H_{11}CH_3-C_7F_{15}COOCH_3$	318	124	.75	.73
$C_6H_{11}CH_3-C_7F_{15}H$	325	140	.69	.68
$CCl_4-C_8F_{16}O$	321	292	.80	78
$CH_3COC_2H_5-C_8F_{16}O$	369	500	.75	.81

Williamson, Scott & Dunlap (49) have recalculated the liquid-vapor equilibria data of Mueller & Lewis (50) and discovered an appreciable discrepancy between their calorimetric heat of mixing and that calculated from the vapor-liquid equilibria data. Williamson & Scott (51) have carefully determined the heats of mixing for this system over the entire composition range at 30° and 50°C.; and, within their one per cent experimental error, find the heat of mixing to be independent of temperature. They combined the vapor pressure data of Mueller & Lewis with their calorimetric heats of mixing to yield the thermodynamically consistent equation for the excess molar free energy given in Equation 12.

$$\tilde{F}^E \text{ cal. mole}^{-1} = x(1-x)\{2020 - 2362T - (70 + 0.148T)(1 - 2x)$$
$$+ (530 - 1.275T)(1 - 2x)^2\} \quad 12.$$

where x is the mole fraction of *iso*-octane. The equation reproduces the excess free energies to 3 cal. mole^{-1} in the range 30–70°.

Dunlap, Bedford, Woodbrey & Furrow (52) obtained the liquid-vapor equilibrium data for the system perfluoro-n-hexane+n-hexane. Three-constant power-series equations of the Guggenheim (4) form

$$\tilde{G} = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 \cdots] \qquad 13.$$

were obtained for the excess thermodynamic functions. The values at 35°C. and $X = 1/2$ of $\tilde{F}^E$, $\tilde{H}^E$ are: 318, 567 cal. mole^{-1}. Williamson & Scott (51) report a value of $\tilde{H}^E = 512$ for this system.

For comparison, coefficients of Equation 13 were deduced from the

available data for three other similar systems which had been previously studied, viz. $n\text{-}C_4F_{10}+n\text{-}C_4H_{10}$, $n\text{-}C_5F_{12}+n\text{-}C_5H_{12}$, and $n\text{-}C_7F_{16}+iso\text{-}C_8H_{18}$, and the ratios of the coefficients A_1/A_0 and A_2/A_0 were compared with corresponding ratios

$$\frac{\bar{V}_1 - \bar{V}_2}{\bar{V}_1 + \bar{V}_2}, \quad \text{and} \quad \left(\frac{\bar{V}_1 - \bar{V}_2}{V_1 + V_2}\right)^2$$

of solubility parameter theory. The Hildebrand-Scatchard equation has been given in the following form by Redlich & Kister (5):

$$\bar{F}^E = \frac{2x_1x_2\bar{V}_1\bar{V}_2(\delta_2 - \delta_1)^2}{\bar{V}_1 + \bar{V}_2}$$
$$\cdot \left[1 - \left(\frac{\bar{V}_1 - \bar{V}_2}{\bar{V}_1 + \bar{V}_2}\right)(x_1 - x_2) + \left(\frac{\bar{V}_1 - \bar{V}_2}{\bar{V}_1 + \bar{V}_2}\right)^2(x_1 - x_2)^2 \cdots \right] \qquad 14.$$

The second term, related to the skewness or tilt of the excess free energy function, is in the predicted direction but about 30 per cent less than that expected on the basis of the difference in their volumes. The authors found that the skewness is more nearly related to $[\bar{V}_1{}^{2/3} - \bar{V}_2{}^{2/3}]/[\bar{V}_1{}^{2/3} + \bar{V}_2{}^{2/3}]$, or their surfaces as proposed by Langmuir (53). The third term, related to the flattening of the free energy function, is more highly temperature dependent (see Equation 12) and considerably larger than expected. In view of these results, one is curious as to the reasons why Equation 11 predicts so well the critical solution compositions such as those shown in Table I.

Dyke, Rowlinson & Thacker (54) have studied the systems of perfluorocyclohexane and perfluoromethylcyclohexane in the corresponding hydrocarbons and the system perfluoromethylcyclohexane with 1,3,5-trimethylcyclohexane. They have measured total vapor pressure vs. liquid composition between 45° and 70°C. for these systems, from which they calculate three coefficients of Equation 13 for the excess free energies. The magnitudes of the coefficients follow the same trend as those of the other fluorocarbon-hydrocarbon solutions discussed above, except that the large values of A_2 appear to be not quite as dependent upon temperature. Of course, A_2 is subject to sizeable experimental error. At 65° and $X = \frac{1}{2}$; $\bar{F}^E$, $\bar{H}^E$, in cal. mole^{-1}, and $\bar{V}^E$ in cm.^{3} mole^{-1} are: $C_6F_{11}CF_3 + C_6H_{12}$, 322, 490, ——; $C_6F_{11}CF_3 + C_7H_{14}$, 322, 690, 7.4; $C_6F_{11}CF_3 + C_9H_{15}$, 340, 500, —. The ratio $\bar{H}^E/\bar{F}^E$ in the second system is very much larger than usual, though $\bar{H}^E$ is supported by two calorimetric values. The gas-liquid critical curve for the second system was found to have a minimum, and when the data are fitted to a quadratic curve of the form $T_c = x_1{}^2 T_{11}{}^c + 2x_1x_2 T_{12}{}^c + x_2{}^2 T_{22}{}^c$, $T_{12}{}^c$ was found to have a value approximately 10 per cent lower than the arithmetic mean of $T_{11}{}^c$ and $T_{22}{}^c$, and this is taken to be indicative of weak 1–2 interactions. The relation between the gas-liquid critical point for mixtures, and intermolecular forces has been discussed by Rowlinson et al. (54).

Reed (55) has modified the regular solution equation for the excess free

energy to account for deviations from the geometric mean law as follows:

$$\bar{F}^E = (x_1\bar{V}_1 + x_2\bar{V}_2)\phi_1\phi_2[(\delta_2 - \delta_1)^2 + 2\delta_1\delta_2(1 - f)] \qquad 15.$$

where $f = f_I f_d f_\alpha$. The terms f_I and f_d have been previously discussed (55) and are $2(I_1 I_2)^{1/2}/(I_1 + I_2)$ and $8(d_{11}d_{22})^{3/2}/(d_{11}+d_{22})^3$, introduced to allow for difference in ionization potentials and sizes of the molecules. Reed (45) has further proposed that weak coupling through van der Waals forces alters the polarizabilities of neighboring molecules when their ionization potentials or characteristic frequencies are very different. This is analogous to the forced amplitudes in weakly coupled mechanical oscillators. The polarizability of a molecule in the mixture is then $\alpha_i^0 + \alpha_{i(j)}$, where $\alpha_{i(j)}$ is an incremental polarizability on molecule i due to the presence of a neighboring molecule j.

$$f_\alpha = \frac{[\alpha_i^0 + \alpha_{i(j)}][\alpha_j^0 + \alpha_{j(i)}]}{\alpha_i^0 \alpha_j^0} \cong 1 + \frac{\alpha_{i(j)}}{\alpha_i^0} + \frac{\alpha_{j(i)}}{\alpha_j^0} \qquad 16.$$

Reed has shown by reasonable argument that the above two correction terms are of opposite sign and that their magnitude depends upon the differences in the ionization potentials of the molecules and the slopes of I vs. P_i, the number of peripheral atoms of kind i surrounding a central group. This relationship has been established (10) for several homologous series. Reed finds principal support of his hypothesis in the composition dependence of the excess molar polarizability calculated from the refractive index and density measurements of Reed & Taylor (20) for three fluorocarbon-hydrocarbon systems. The excess molar polarizability is negative in the hydrocarbon-rich solutions and positive in the fluorocarbon-rich solutions. This peculiar behavior appears to be well outside the experimental error. As additional evidence, f_α was shown to be less than unity for solutions of fluorocarbons and hydrocarbons, thus increasing the calculated excess free energy; and greater than unity for solutions of carbon tetrachloride with fluorocarbons, thus cancelling the effect of f_I and f_d, and offering an explanation as to why Equation 10 works so well for these cases. Perturbation of the polarizability is a new idea in solution theory and needs verification both theoretically and experimentally. Especially valuable would be verification of Reed's ionization potentials of fluorocarbons, upon which the hypothesis depends.

Yen & Reed (56) found that the system perfluoro-n-heptane+perfluorocyclic oxide obeyed Raoult's law over the entire composition range and that the excess volume was negative.

Chlorofluorocarbon solutions.—Yen & Reed (56) obtained liquid-vapor equilibrium data at 1 atm. pressure for the systems 1,2-dichlorohexafluorocyclopentene ($C_5Cl_2F_6$) + 2,2,3-trichloroheptafluorobutane ($C_4Cl_3F_7$); $C_5Cl_2F_6$ + $C_8F_{16}O$, $C_4Cl_3F_7 + C_8F_{16}O$, and $C_4Cl_3F_7 + n$-C_7H_{16}. These compounds form an intermediate class between the perfluorocarbons and hydrocarbons. The first system forms an ideal solution; the next two are non-ideal but their properties can be predicted rather well by solubility parameter theory,

using only the δ's. The hydrocarbon system shows a sizable deviation from the theory, requiring a correction equivalent to $f = 0.97$ in Equation 15. All solutions show an increase in volume on mixing.

Smith, Walkley & Hildebrand (57) determined the solubility of iodine between 0° and 35°C. in n-2,2,3-$C_4Cl_3F_7$ and in mixtures of carbon tetrachloride with perfluoro-n-heptane. Also determined were the partial molal volumes of Br_2 and I_2 in several solvents including three chlorofluorocarbons, and in two mixed solvents $CCl_4 + n$-C_7F_{16} and c-$C_4Cl_2F_6 + CCl_4$, over a range of concentration. Solubilities are in agreement with solubility parameter theory. The partial molal entropy of solution of liquid iodine in $C_4Cl_3F_7$ is 5 cal. mole^{-1} deg. greater than $-R \ln x_2$ as previously found with many other solvents (58). The partial molal volumes increase with decreasing solubility as expected, but $\bar{v}_2$ for bromine in the mixed solvents is less than an additive function of its values in the two pure components.

Smith & Hildebrand (59), in further work in this area, have measured $(\partial P/\partial T)_v$ for n-C_7F_{16}, c-$C_6F_{11}CF_3$, c-$C_4Cl_2F_6$, n-2,2,3-$C_4Cl_3F_7$, $CCl_2F \cdot CCl_2F$, and CCl_4. Walkley & Hildebrand (60) determined the partial vapor pressure of iodine over its solutions in CCl_4 and CS_2 in order to assess the deviations from Henry's law as used in calculating the entropy of solution of iodine in these solvents. Previously, these values had been obtained from regular solution theory and the properties of liquid iodine extrapolated to 25°.

Neilson & White (61) determined calorimetrically the heat required to evaporate completely a certain quantity of a mixture of chlorodifluoromethane with dichlorodifluoromethane, from which they calculated the heat of mixing. At $X = \frac{1}{2}$ and 222° K. $\tilde{H}^E$ is 115 cal. mole^{-1} and $\tilde{V}^E$ is 0.58 cm.^{3}. The polarity of the hydrogen compound is probably responsible for the observed behavior.

Hydrocarbon solutions—Ultimately, the more quantitative theories of solutions will have to recognize and deal with all of the interactions between all of the particles in the mixture. In order to accomplish this, much assorting will have to be done. This year a series of valuable papers appeared that are concerned with empirical and semi-empirical methods for correlating the properties of solutions with molecular structure. A group interaction model was described by Redlich, Derr & Pierotti (62), in which a molecule is divided into various characteristic groups, viz. CH, CH_2, CO, etc. The frequency of contacts between the various groups in the system depends upon the concentration and characteristic cross sections of the groups. Thus, if a molecule i contains $m_i{}^u$ groups of type u, and a molecule j contains $m_j{}^v$ groups of type v, the frequency of a uv contact is proportional to $m^u{}_i m_j{}^v n_i n_j s^u s^v$ where the s^u and s^v are the characteristic cross sections.

With appropriate sets of characteristic group cross sections, and group interaction coefficients, k^{uv}, the relative energy content of the system can be calculated.

Papadopoulos & Derr (63) have tested the group interaction model on

binary solutions of hydrocarbons. Group volumes were obtained from a study of the molal volumes of hydrocarbons, assuming that the volume is the sum of its characteristic groups. Their assignments represent the volumes of over 1000 hydrocarbons within 1.5 per cent. Group cross sections were taken as proportional to the $\frac{2}{3}$ power of the group volumes. Characteristic group interaction coefficients were derived from the partial molal enthalpies of mixing at infinite dilution obtained from calorimetric studies or from the temperature derivatives of the free energies. Data for a number of binary mixtures were correlated rather well with a surprisingly small number of interaction coefficients.

Pierotti, Deal & Derr (64) have devised a scheme for estimating the excess partial molar free energies at infinite dilution by treating the excess free energy as a sum of interactions between pairs of structural groups. Five terms are used to allow for interactions predominantly between 1-2 functional groups, 1-1 functional groups, a coefficient independent of the functional groups, and a small corrective term depending on the nature of the solvent.

Dixon (65), in an elaborate study of the principle of congruence [Bronsted & Koefoed (66)], reported the densities, viscosities, and refractive indices of 16 equimolar solutions and 21 pure hydrocarbons. The properties of pairs of hydrocarbon liquids containing equal ratios of hydrocarbon segments were systematically compared and arranged into three characteristic groups. For example, an equal molar mixture of 2,5-dimethylhexane+2,2,4-trimethylpentane had nearly the same density, visosity, and refractive index as an equal molar mixture of 2,4-dimethylpentane +2,2,5-trimethylhexane. These liquids are classified as congruent liquids. A second group, classified as noncongruent liquids, exhibits a much wider difference in each of the three properties. A third class was found to exhibit congruency with respect to density and refractive index but were noncongruent with respect to viscosity. A large enough variety of structures was compared to conclude that molecular symmetry had negligible effect. The only difference between the first two classes was that pairs exhibiting noncongruency contained one component with adjacent branched carbon atoms, e.g., 2,3-dimethylbutane. It appears as though the rotational barrier, which is larger at the bond between adjacently branched carbon atoms than between methylene groups, is responsible for the noncongruent behavior. The behavior of the third class is attributed to the difference in mass distribution.

The studies support the proposal of Schiessler (67) that there is very little molecular order in liquids containing saturated hydrocarbon molecules over most of their liquid range. Dixon states, "It is difficult to envision how molecules in an equal molar mixture—e.g., 1,2-dicyclohexylethane and n-tetradecane—can reproduce any short- or long-range intermolecular ordering that might occur in a liquid containing a single molecular species like n-octylcyclohexane."

Goates, Sullivan & Ott (68) determined calorimetrically the heats of mixing for the three binary solutions that can be formed from carbon tetrachloride, cyclohexane, and benzene. These data were combined with free energy data from the literature and self-consistent functions for the free energy were derived, from which all of the thermodynamic properties at constant pressure can be calculated. Values of $\bar{F}^E$, $\bar{H}^E$, and $\bar{S}^E$ at 25° and $x = \frac{1}{2}$ are: $CCl_4 + C_6H_{12}$, 17.8, 40.2 cal. mole^{-1} and 0.078 e.u.; $C_6H_{12} + C_6H_6$, 74.8, 182, 0.358; $CCl_4 + C_6H_6$, 19.6, 26.0, 0.215.

The temperature dependence of $\bar{H}^E$ for the carbon tetrachloride + benzene system was suggestive of compound formation, which was verified by a phase study. A 1-1 compound was formed which crystallized from the melt at $-39°C$. In order to test the assumption that π bonding is responsible for the formation of the complex, they determined the phase diagram with toluene; the methyl group should enhance the electron density of the benzene ring. The 1-1 compound formed, melted at $-5°$. No evidence of compound formation was found in the system carbon tetrachloride + nitrobenzene, and chloroform did not form a complex with p-xylene. Calorimetric heats of mixing were obtained for two ternary systems, viz. benzene + cyclohexane + carbon tetrachloride, and carbon tetrachloride + methylene chloride + chloroform.

Ehrett & Weber (69) found the system n-hexane + methylcyclopentane to be ideal over the pressure range 200 to 760 mm. Hg. Nielsen & Weber (70) obtained liquid-vapor equilibrium data for the binary systems: ethyl alcohol + benzene and benzene + n-heptane and for the ternary system of these three.

Berry & Sage (71) determined partial molal volumes for the methane + cyclohexane system between 70°F. and 340°F. and from the bubble point to 10,000 p.s.i. Reamer & Sage (72) have carried out similar studies for methane with n-heptane. Weber (73) has calculated the saturated liquid phase enthalpies for the system ethane + n-heptane at 100 p.s.i. intervals between 100 and 600 p.s.i. from Kay's PVT data (74).

Price & Kobayashi (75) have determined the liquid-vapor equilibrium for the system methane + propane from 50°F. to $-200°F$. and together with Leland (76) have smoothed the data using the Benedict-Webb-Rubin equation of state.

McLaughlin & Zainal (77) determined the solubilities in benzene between 25° and 80°C. for diphenyl, o-, m-, and p-terphenyl, 1,3,5-triphenylbenzene, naphthalene, anthracene, phenanthrene, pyrene, triphenylene, chrysene, fluoranthene, fluorene, and acenaphthene. For all of the compounds that melted below 150°C. the solubilities can be expressed by the relationship $\ln x = -13.8/R \ [T_f/T - 1]$ where T_f is the melting point. In other words, all of these substances have the same solubility in benzene at the same "reduced" temperature T_f/T. The coefficient in the above equation may be compared with the average entropy of fusion, which for these substances is 13.0 ± 0.6 e.u.

Chaujavek & Van Winkle (78) determined the liquid-vapor equilibria for the system styrene+ethylbenzene at five pressures between 10 and 200 mm. and found the system to be ideal within experimental error. Troutner (79) determined the solid-liquid equilibrium diagrams for all of the binary and ternary mixtures of biphenyl, o-terphenyl, m-terphenyl, naphthalene, and phenanthrene in addition to some melting point data on quaternary and quinary mixtures.

MacWood & Paridon (80) determined the liquid-vapor equilibria for the system ethyl ether+diborane at 25, 50, and 100 p.s.i. Papousêk & Smékal (81) determined the liquid-vapor equilibria for the system ethyl ether+n-butyl ether at atmospheric pressure. The van Laar constants, calculated from the energies of vaporization, molar volumes, and parachores of the pure components by the method of Erdös (82), were in agreement with the data. Papousêk & Págo (83), from a study of liquid-vapor equilibria at 600 mm., found that ethyl ether and dibutyl ether form ideal solutions with anisole, and methyl alcohol with tetrahydrofuran exhibits positive deviations from Raoult's law.

Alcohols.—Black (84) has assimilated most of the available liquid-vapor equilibria data in the literature, both isothermal and isobaric, for the first five n-alcohols with benzene, methanol with toluene, and ethanol with toluene, methylcyclohexane, and n-heptane. Activity coefficients were calculated as rigorously as available data permitted, correcting for gas imperfections and the effect of pressure on the chemical potential of the liquid. The data were represented by modified van Laar equations. Excess thermodynamic functions were calculated and the enthalpies of mixing were compared with calorimetric data in the literature. The agreement is remarkable considering the number and magnitude of the corrections involved, and the asymmetry of the enthalpy from the rather symmetrical excess free energy functions. Although most of the values shown are in agreement to within about 4 per cent, recent calorimetric data on the system ethyl alcohol+benzene by Williamson & Scott (51) suggest a review of this system. At 55°C. and $x=0.3$ (near $\tilde{H}^E$ max.) Black calculates $\tilde{H}^E=223$ cal. mole^{-1}. Williamson & Scott (51) have measured 272 cal. mole^{-1} at 45°C. The enthalpy functions appear to be independent of temperature in this region. Williamson & Scott also determined $\tilde{H}^E$ for methanol in benzene at 25° and the values were in agreement with Black's calculations.

Papousêk, Papousêk & Págo (85) in their study of the liquid-vapor equilibria for the systems of carbon tetrachloride with n-propyl alcohol and iso-propyl alcohol, found that functions based on the Kretchmer-Wiebe (86) theory of continued association could represent the thermodynamic data satisfactorily. The theory predicts the shape of the excess free energy curves correctly, indicating less pronounced association of iso-propyl alcohol when compared with n-propyl alcohol.

Brown & Smith (87) obtained isothermal vapor-liquid equilibria data for the systems n-propanol+benzene and n-butanol+benzene at 45°.

The former system forms an azeotrope, while none was observed for the latter to 0.01 mole per cent butanol. Bures, Cano & de Worth (88) measured the liquid vapor equilibrium for the system 2-propanol+2,2,4-trimethyl-pentane. Tooke (89) determined liquid-vapor equilibria for several alliphatic alcohols with aryl hydrocarbon solvents. These include n-butanol with toluene, ethyl benzene, and n-propyl benzene; and 2-butanol with benzene, toluene, and ethyl benzene.

McKinney, Skinner & Stavely (90) have measured the coefficients of expansion and isothermal compressibilities at 0°C. from which they derive $(\partial S/\partial V)_T$ for the normal primary alcohols from methanol to octanol. $(\partial S/\partial V)_T$ is a measure of the increase in entropy per unit volume, and consequently might be expected to be a simple function of the number of carbon atoms. They found, however, an alternation effect in this property for the first four-carbon alcohols, then a steady increase with increasing chain length.

Aqueous solutions.—The solubility of water in benzene was determined recently by Alexander (91) in the range 0–65°C., and by Arnold *et al.* (92) in the same range. The minimum in the temperature-solubility curve near 15°C., first observed by Bohon & Claussen (93), was confirmed by both; yet the solubilities measured by Alexander, which are in agreement with Bohon & Claussen, are some 3 to 5 per cent higher than the solubilities of Arnold *et al.*

Lu (94) has re-evaluated the liquid-vapor equilibrium data of Bosjna-kovic & Grumbt (95) for the ethanol+water system, and expresses the activity coefficients in the Redlich-Kister form (5). Barr-David & Dodge (96) have determined the liquid-vapor equilibria for the systems ethanol+water and 2-proponol+water between 150° and 350°C. Horyna (97) studied the aniline+water system up to 16 atm.

Chew & Orr (98) determined the ternary phase diagram for the system water+n-propyl alcohol+hexamethyldisiloxane at 25°C.

Hydrogen bonding.—Until this year chloroform was the only substance known, at least to this writer, containing a hydrogen bonded to carbon that could form hydrogen bonds with other polar substances. Mastrangelo (99) has studied the solubilities of $CHCl_2F$, $CHClF_2$, CH_2ClF, CHF_2CHF_2, and CHF_2CClF_2 over a range of temperature and pressure in tetraethylene-glycol dimethylether. All of these substances participate in hydrogen bonding to some degree with the solvent. A quasi-chemical model was suggested to correlate the data. The solvent is regarded as containing a number, f, of identical energetically favorable sites, the maximum number per molecule in this case being five. For the first three solutes, the best fit for the model proposed was found using $f=3$. The solubilities of the others were correlated with $f=2$. Mastrangelo suggests that incomplete saturation of the available sites may be due to steric hindrance or deactivation. As an additional test of the quasi-chemical model, the data for chloroform+acetone gave a value $f=1$.

An even more exciting example of this phenomenon was discussed by Williamson & Scott (100), who found that the heat of mixing for the system 1-hydroperfluoroheptane+acetone was negative in the acetone-rich solutions and positive in the fluorocarbon-rich solutions.

Mukherjee & Grunwald (101) measured the dielectric constants, densities, viscosites, and the boiling point-composition diagram for the system ethanol+2,2,2-trifluorethanol. This system has a maximum boiling point indicating strong intermolecular bonding. A minimum in the viscosity composition curve is attributed to the formation of mixed complexes affecting the self-association equilibria in such a way that the overall average of the degree of association is lowered.

GASES IN LIQUIDS

Walkley & Hildebrand (102) determined the partial molal volumes of hydrogen and deuterium in benzene, toluene, and perfluoro-n-heptane, and found that the values for hydrogen were 10 per cent larger than those of deuterium in the hydrocarbon solvents, and larger by about 2 per cent in the fluorocarbon. They expect that the difference will be explained when the different zero point energies of hydrogen and deuterium are considered.

Alexander (103), using a microcalorimeter, measured the heats of solution of the rare gases in water at 25°C. The values in kcal. mole^{-1} are: neon, -1.4; argon, -2.88; krypton, -3.69; and xenon, -4.29. These values are in substantial agreement with previous values obtained from the temperature coefficient of solubility. Himmelblau (104), using data from the recent literature on the solubilities of O_2, N_2, He, and Xe in water, obtained three-constant equations which fitted the data within a few per cent over a wide temperature interval. The partial molal entropies of solution in water are more negative than in nonpolar solvents.

Reed & McKetta (105) determined the solubility of butadiene in water at 100°, 160°, and 220°F. from the vapor pressure of water to the pressure at which the hydrocarbon-rich phase appeared. Azarnoosh & McKetta (106) did likewise for propylene in water.

Gjaldbaek & Niemann (107) studied the solubilities of nitrogen, argon, and ethane in the first five primary aliphatic alcohols, cyclohexanol, ethylene glycol, and water. All solvents have essentially the same dipole moment (1.8 debye). They found the solubility of ethane to be 360 times greater in pentanol than in water. In a later article (108), they reported the solubilities of argon and ethane to be larger in carbon disulphide than in perfluoro-n-heptane, and that ethane is the more soluble in both solvents.

Williams (109) determined the solubility of N_2 in $CFCl_2CF_3$, and Ellis (110), the solubility of CO_2 in water up to 350°C. Reamer & Sage (111) determined the composition of the gas phase of the N_2+NH_3 system; and, combining their results with the bubble point data of Wiebe & Gaddy (112), established the compositions of the coexisting phases between 40° and 250°F. up to 6000 p.s.i. They also determined the composition of the coexisting gas

and liquid phases for the system $H_2 + NH_3$ (113), covering the same range.

Shade, Cooper & Gilbert (114) measured the solubility of methylsilane in methyltrichlorosilane between $-20°$ and $50°C$. The system exhibits positive deviations from Raoult's law.

Johnson & Shuttleworth (115) determined the solubility of krypton in liquid lead and liquid tin, and noted a correlation between solubility and the surface tension of the metals.

METALLIC SOLUTIONS

Speiser & St. Pierre (116) discussed the application of the Gibbs-Duhem equation to the determination of activities and the location of phase boundaries, by studying the vapor composition as a function of the composition of the condensed system at a given temperature and pressure, noting that this method is particularly suited to systems whose vapor pressures are too low to be measured precisely.

Kleppa & Thalmeyer (117), in continuance of their investigations on binary alloys in liquid zinc, report thermodynamic data (e.m.f.) for zinc-rich alloys of Cu, Ag, Ga, Ge, Sb, and Bi. They found a semi-quantitative correlation between the partial molal entropy of the solvent and the electron concentration (valence electrons per atom) in the solution. $\bar{H}^E$ is positive and in the order ZnSb > ZnSn > ZnIn > ZnCd > ZnAg. ZnAg has a negative excess enthalpy. The curvature of the excess enthalpy-composition function at low solute concentration is opposite to that predicted by Friedel's (118) theory.

Aronsson & Lundgren (119) carried out x-ray studies on the ternary systems of Mn+Si+B, Fe+Si+B, and Co+Si+B, and found intermediate binary and ternary phases at $1000°C$. Hall (120) determined the phase diagram for the system Ag+Mn+Al at $400°$ and $600°C$. Bowersox & Leary (121) determined the solubility of plutonium in mercury between $20°$ and $325°C$. The solubility increased from 2 gm. per liter to 85 gm. per liter over this range.

Borg (122) measured the vapor pressure as a function of temperature for solid cadmium and five solid cadmium-magnesium alloys, and calculated the activity coefficients. Wittig (123) determined the heats of mixing for Zn, Cd, In, Tl, Sn, and Pb with Bi; and Wittig & Müller (124), for the systems Bi+In, Bi+Tl, and In+Te. The heat of mixing is most negative when two metals are in the same period, and most positive when they are separated as far as possible in the periodic table.

Espagno, Azou & Bastien (125) carried out a dilatometric study of the system zirconium+hydrogen, showing two solid solutions by the temperature derivative for the coefficient of expansion. Bibring & Manenc (126) carried out an x-ray study on the Co+Ti system in a cobalt-rich region. A solid solution exists in two allotropic forms, hexagonal close-packed, and face-centered cubic; the latter is more stable.

Kendall & Haltgren (127) measured the heats of formation of solid solutions of tin in lead at 400°K. by liquid tin calorimetry. The partial molar heat of liquid lead in tin is 1490 cal. gm. atom^{-1} at 612°K. These data, together with the phase diagram, were combined with previous thermodynamic measurements to produce a self-consistent thermodynamic description of the system.

Scace & Slack (128) determined the solubility of carbon in liquid silicon in the range 1560 to 2900°C., and proposed a phase diagram for this system. The enthalpy of solution is 53 ± 3 kcal. mole^{-1}. SiC decomposes peritectically at 2830°C. into a melt of 19 atomic per cent carbon. Some data for the solubility of carbon in germanium were given.

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SURFACE CHEMISTRY

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Introduction

In order to minimize overlap with the chapter on colloids appearing else-where in this volume, this review will deal mainly with gases or vapors in interaction with solid surfaces. The choice of topics, indicated by the major headings, is intended to reflect the areas in which the most significant de-velopments have occurred during the past year, although this has un-doubtedly been colored by personal tastes. As in previous years there has been no spectacular breakthrough, although major progress is being made in the spectra of adsorbed species and in the electrical properties of surfaces, particularly with the field-emission microscope. It is a tribute to the older indirect methods that the intimate examination of individual adsorbed molecules now possible has occasioned no real surprises; and many questions remain to which the classical methods may profitably be applied.

The bibliography dates from the close of last year's article by Honig (1) in this series, and extends approximately through December of 1959. Owing to the lag in translation, several important Russian and Japanese articles have been available only in abstract form. Perhaps even more frustrating than the lack of a common language is the fact that relevant papers are scattered throughout scores of periodicals which in turn are widely dis-persed among the branch libraries. It should at least be possible to adopt a single journal in each language as an outlet for this important field.

The past year has witnessed the appearance of Volume **VI** of Emmett's *Catalysis* (2) and Volume **XI** of *Advances in Catalysis* (3). Other new books include *Fine Particle Measurement—Size, Surface and Pore Volume* by Orr & Dallevalle (4), *Catalyse Hétérogène* by Germain (5), a revised edition of *Surface Chemistry* by Bikerman (6), and a German translation by Vogen (7) of Roginski's *Adsorption und Katalyse an inhomogen Oberflächen*. The latter two books have been critically reviewed by Taylor (8) and Schwab (9). Under the subject of gas chromatography, mention should be made of the publication of the proceedings of the second symposium (Amsterdam) edited by Desty (10), the second edition of Kuelemans' monograph (11), and a new volume under the editorship of Pecsok (12).

The following review articles are particularly relevant: Culver & Tomp-kins (13), "Surface Potentials and Adsorption Processes on Metals"; the Kendall Award Address by Emmett (14), "Adsorption and Catalysis"; Zettlemoyer (15), "Modern Techniques for Investigating Interactions with Surfaces"; Moesta (16), "Der Einfluss adsorbierter Gase auf physikalische Eigenschaften der Oberfläche fester Körper"; Sheppard (17), "Infrared Spectra of Adsorbed Molecules"; T. Vol'kenshtein (18), "Electron Theory of

Catalysis on Semiconductors"; F. F. Vol'kenshtein (19), "Modern State of Electronic Theory of Catalysis on Semiconductors"; Kemball (20), "Catalytic Exchange of Hydrocarbons with Deuterium"; and Taylor (21), "Radiation Effects on Solids, Including Catalysts." Such subjects, so recently reviewed, can be given little more than passing mention here.

Also during 1959 three symposia were held under the titles: "Recent Advances in the Study of Contact Catalysis" (22); "Thirty-Third National Colloid Symposium" (23); and "Reaktionen zwischen Metallen und Gasen" (24).

NATURE OF THE ADSORBENT SURFACE

Surface area.—In an attempt to arrive at a self-consistent set of molecular cross sections, Kodera & Onishi (25) have given the values listed in Table I for various gases adsorbed on carbon blacks. They recommend using

TABLE I

Molecular Cross Sectional Areas (A^2)

Gas	t°C.	vdW	Liquid	Livingston (26)	Kodera & Onishi (25)
N_2	−196	15.4	16.2	15.4	14.2
A	−196	13.6	13.8	14.6	13.8
A	−183	13.6	14.4	15.5	14.4
O_2	−183	13.5	14.1	14.6	13.5
CO_2	− 78	16.5	17.0	19.5	20.8
n-C_4H_{10}	0	33.0	32.1	44.6	38.6

argon as a standard, presumably in conjunction with the Brunauer-Emmett-Teller (BET) value of v_m determined on the basis of the saturation pressure of the supercooled liquid. Until wider agreement is reached on the best values of the cross sectional areas, it might be safer merely to quote ratios: e.g., $\sigma_{N_2}/\sigma_A = 1.14$. The question of the correct saturation pressure to use for argon below its melting point has been examined by Danes & Nováková (27); they find that expressing the relative pressure in terms of the supercooled liquid generally leads to better agreement with argon isotherms at other temperatures and with other gases. The molecular cross sections they employ are: nitrogen, 16.2 A^2; argon (78°K.), 16.6 A^2; and argon (90°K.), 18.2 A^2.

Tomlinson (28) reports that the surface-area values determined by krypton adsorption following the method of Beebe *et al.* (29) lie some 5 to 7 per cent below those measured by nitrogen adsorption. Malden & Marsh (30) observe that in a large majority of cases the BET plots for krypton adsorbed on some 50 low-area catalysts are convex to the relative pressure axis, and are thus of limited value for surface area determinations. No corre-

lation was found between this convexity and the isosteric heats of adsorption. Fejes, Kiraly & Schay (31) have employed a simplified method for the calculation of specific surface area from isotherm measurements of the adsorption of furan at 23°C., and find agreement with the BET method within four per cent on eight different adsorbents. Based on nitrogen surface areas measured at 90°K., the molecular cross-sectional areas for butane and isobutane at 0°C. and for furan at 23°C. are respectively 53, 54, and 42 A². These magnitudes differ from those expected from the bulk liquid density in such a direction as to suggest a preferred orientation on the adsorbent surface. For alumina, silica, and aluminosilicates, Dobychin & Zellinskaya (32) show that a monolayer of benzene is adsorbed at $p/p^o = 0.214$, which is thus the basis of a rapid surface-area method. Hooley (33) has determined the surface areas of carbon blacks by adsorption of bromine, and reports isosteric heats of 11 kcal./mole. Bromine isotherms on graphites have also been studied by Funasaka et $al.$ (34).

The work of Boehm & Gromes (35) is remarkable for the discovery of multilayer (type II) isotherms for phenol adsorbed from nonpolar solutions onto hydrophilic surfaces, in contrast to the unimolecular behavior of hydrocarbons observed by Smirnova & Topchieva (36). The phenol isotherms are rectified in the standard BET plot, using the concentration relative to the concentration at the solubility limit in place of relative pressure, and yield a phenol cross section at 20°C. of 40.2 A² relative to 16.2 for nitrogen. On carbon, however, Wheeler & Levy (37) find that phenol and cerain of its o-alkyl derivatives appear to occupy areas ranging from ~6 to 60 times their expected molecular areas.

The radiometric method of determining surface area has been applied by Protashchik (38) to MgO through the chemisorption of radioactive CO_2. A modification of this classical method has been studied by Sinitsyna et $al.$ (39, 40), in determining the specific surface of $Mg(OH)_2$ in various states of dehydration by the rate of emanation of thoron from radiothorium in the sample.

Kaganer (41) has applied a modification of the Dubinin-Radushkevich (42, 42a) equation at relative pressures $p/p^o < 0.01$. This equation has the form $\log v/v_m = -D(\log p/p^o)^2$ so that a plot of $\log v$ versus $(\log p/p^o)^2$ has slope $-D$ (characteristic of the adsorbent) and an (extrapolated) intercept $\log v_m$. The resulting v_m values agree with those from the BET method within ± 2 per cent. Schreiber & Waldman (43) have reported a rapid semi-qauntitative method for determining the surface area by measuring the heat of adsorption by differential thermal analysis when the sample is exposed to the saturated vapor of any one of several liquids, e.g., water, n-butane, or ethyl chloride.

Pore and surface structure.—Takamura (44) has found that the specific heat curves for benzene adsorbed on silica gel have peaks below the normal melting point of benzene, although the calculated latent heat of fusion is the same as for bulk benzene, indicating a capillary condensation in multilayers.

An examination has been made by Gärtner & Griessbach (45) of the relative
BET surface areas of microporous silica gels towards polar and nonpolar
molecules of various sizes and as a function of thermal aging. The available
surface towards a given adsorbate goes through a maximum as the pore size
decreases. In their studies of the pore structure of thin (<1000 A) films on
optical surfaces, Dobychin & Pogodaev (46) have developed a static appara-
tus capable of measuring surface areas $\sim$100 cm.^{2} using adsorbents in
amounts <1 mg. Zalevski & Bykov (47) have investigated the regime of
large pores by introducing mercury under pressure, and present pore size
distributions for numerous natural mineral adsorbents.

In an attempt to elucidate the pore structure of active carbon, Wolff (48)
has examined the penetration by liquids having different molecular shapes
by measuring the desorption of nitrogen displaced in the process. The dis-
crimination against all but the smallest molecules permits an estimation of
the micropore widths, which turn out to be remarkably constant ($\sim$7 A).
In a subsequent paper, Wolff (49) proposes a model for the structure of ac-
tive carbon and a mechanism for its formation based on a random oxidative
attack on individual graphitic planes. On the basis of this model, which differs
from that proposed earlier by Cadenhead & Everett (50), he derives a rela-
tionship between the specific surface area and the micropore density that
appears to correlate the available data. Gunn (51) has employed low-angle
x-ray scattering to determine the Debye correlation distance for several
petroleum catalysts and has found this to be a practical method of charac-
terizing the performance quality and adsorption surface area. The question
of the nucleation of solid-gas reactions, which will one day have to be
faced, has been underlined in the work of Asselmeyer & Riedel (52) who
find the resistance of polished rock salt surfaces to attack by water vapor
to be increased by factors $\sim$10^6 by baking for an hour at 4–500°C.

Effects of irradiation.—Certain gaseous fission products, notably Xe^{135},
act as pile poisons because of their large neutron capture cross sections.
Amphlett & Greenfield (53) have examined the effect on the high tempera-
ture adsorption of Kr and Xe of irradiation of a charcoal adsorbent with
$\sim$10^{11} rads of 1 Mev electrons. They find an increase in adsorption at 100°C.
but little change at 20°C. The penetration of metals by energetic rare gas
ions has been examined experimentally by Carmichael & Trendelenburg
(54) and by Ehrlich & Hudda (55), and theoretically by Kuchai & Rodin
(56). Continued bombardment leads to a kind of steady state re-emission
of the trapped atoms. The theoretical treatment appears properly to ac-
count for the observation that the total amount of gas accumulated per
unit area of the bombardment surface approaches a saturation limit, even
in thick plates, and that almost all of the gas is found at depths of the
order of the range of the ions. Honig (57) has found that the sputtered par-
ticles resulting from the bombardment of Ag and Ge surfaces with low energy
rare gas ions have energies below five ev. This result is consistent with the
observation by Koedam (58) that the sputtering threshold energy should
lie below 20 ev.

Adsorption and crystal development.—This general subject has recently been reviewed by Bliznakov (59), who has also been active in experimental work (60). Theoretical considerations on the effects of impurities on the equilibrium and growth forms of idealized simple-cubic homopolar crystals have been given by Lacmann & Stranski (61). Hartman's (62) detailed treatment, in terms of the surface and interaction energies, indicates that the [110] face of nonionic crystals is enhanced if adsorption occurs at step edges only. Effects in ionic crystals are larger and can lead to abnormal development, particularly in those high-index faces [e.g., (123), (137) of fluorite] parallel to the direction in which the interaction energy of the crystal ionic chains is zero. Perry (63) has observed that the organic polymer in which AgBr-AgI suspensions are made can influence both the ease and morphology of crystal growth. Overgrowth and epitaxy of Ag on cleavage faces of rock salt have been studied by Vermout & Dekeyser (64) and related to imperfections in the substrate surface.

Two forms of oriented crystallization of supercooled water on oriented crystals of Ag supported on muscovite have been observed by Jaffray & Montmory (65) to both correspond to union of the [0001] and [111] planes respectively. No similar simplicity appeared in the oriented growth of ice crystals on AgI. Seifert (66) has produced oriented crystallization of polypeptides on quartz surfaces. The accommodation to deformation of various thin (300 to 700 A), oriented, metallic films has been examined by Brame & Evans (67) using electron microscopy. The experiments of Morlin (68) on NaCl suggest that the Joffe effect, according to which the solution of the surface layer of a crystal improves its plastic properties, may be due to sources of slip. The production and characteristics of thin inorganic films formed under vacuum evaporation have been summarized by Ross (69).

PHYSICAL ADSORPTION

Adsorption isotherms and equation of state.—Hill (70) has compared several different definitions of physical adsorption and finds considerable differences in the effective solid-gas molecular potentials. He also derives the exact two-dimensional virial expansion for the Gibbs formulation and shows that this does not lead to a law of corresponding states. In their studies of gas imperfections near solid surfaces, Halsey and co-workers (71, 71a, 71b) have customarily employed a hard-sphere model with a $1/R^3$ attractive potential and have assumed classical statistics. Hansen (72) has evaluated the second virial coefficient for gas-solid interaction including correction for quantum effects, employing the traditional Lennard-Jones 12-6 pair potential. He finds that a small, but possibly observable, quantum effect is to be expected for helium on carbon black at 78°K. He also attempts to take account of the contribution made by pre-adsorbed molecules on the adsorbate imperfections. Considerations similar to those of Halsey *et al.* have been applied by de Boer & Steggerda (73) in relating the "helium-density" to the true density for microporous solids. In a detailed study of the interaction of krypton with several metals, Pierotti & Halsey (74) have employed the isotherm equation

previously developed by Singleton & Halsey (75). This isotherm proves remarkably useful in the evaluation of the energy of interaction of the adsorbed molecule with the surface. Redlich & Peterson (76) have proposed an empirical isotherm equation in the form $v = Ap/(1+Bp^g)$, which has the useful property of approaching a linear form for small pressures and the form of the Freundlich isotherm for high pressures. The excellent fit to the adsorption isotherms of n-pentane on molecular sieves at various temperatures is adduced in support of this isotherm. In a review of various isotherm equations, A. V. Kiselev (77) has employed the quasichemical method to derive two new isotherms: for monolayers, $\theta/x(1-\theta) = K_1 + K_1 K_2 \theta$; and for multilayers, $\theta(1-x)^2/x[1-\theta(1-x)] = K_1 + K_1 K_2 \theta(1-x)$, where θ is the fractional coverage, x the relative pressure, and K_1 and K_2 are "equilibrium constants" appropriate to the method. In a subsequent paper (78), these theoretical isotherms are shown to agree satisfactorily with experimental adsorption data, through the monolayer region and above the critical temperatures, for a wide variety of systems. An attempt has been made by Iagodovskii (79) to apply Kiselev's monolayer isotherm to the reversible part of the benzene adsorption by palladium films, with some success.

Employing the modified van der Waals equation introduced by Hirshfelder *et al.* (80), Barrer and co-workers (81, 82) have arrived at the equation of state,

$$\left[P + \frac{n}{12}\left(\frac{a}{V^2} + \frac{a'}{V^3}\right)\right](V - b + b'/V) = RT,$$

for fluids having coordination number n adsorbed within porous crystals. This equation and the adsorption isotherms calculated therefrom successfully describe the adsorption of argon in Ba-faujasite and nitrogen in K-faujasite over a considerable temperature range. One remarkable feature is the high intracrystalline pressures—perhaps several hundred atmospheres—permitted by this equation of state.

Physical properties.—Using NMR techniques, Winkler (83) has found that for coverages below one monolayer of water on alumina, both the longitudinal and transverse NMR relaxation times are proportional to the amount adsorbed. From the transverse relaxation time in a monolayer compared with that in a macropore phase, he calculates a micropore volume that compares favorably with those measured from the adsorption isotherms of nitrogen and benzene. Zimmerman & Lasater (84) have found NMR evidence of two-phase behavior of water adsorbed on silica gel. They cautiously suggest that an abrupt decrease in the nuclear correlation time may signal the completion of a monolayer. Using the same alumina samples employed by Winkler, Ebert (85) has measured both the dielectric constant and the apparent dielectric loss factor as functions of the amount of water adsorbed. While the dielectric-constant isotherms are smooth, the loss factor isotherms show discontinuities in slope that are interpreted in terms of changes in the state of the adsorbed phase from monolayer to multilayer or capillary adsorption. Since the attenuation is greatest when the relaxation time corre-

sponds with the reciprocal of the frequency of the electric field, one can obtain the mean residence time in the adsorbed monolayer in terms of the observed frequency at which the dielectric loss becomes significant. In this way, Ebert calculates an energy of adsorption of 14.5 kcal./mole for water on alumina. Odajima, Sohma & Watanabe (86) also have combined NMR and dielectric constant studies of water adsorbed on fibrous materials. They observe three distinct states, one corresponding to localized adsorption, and two others to mobile adsorption, depending upon the moisture content. Dielectric studies have also been made for water on silica gel by Kamiyoshi & Ripoche (87), for ethanol on alumina gel by Shimizu (88), for ammonia on silica gel by Felden (89), and for methyl and ethyl alcohols and water on a variety of powdered adsorbents by Thorp (90). In all these cases there is evidence for distinctly different behavior for the adsorbate in monolayers and in multilayers or capillary condensation. Thorp particularly has found hysteresis loops in the adsorption-desorption isotherms of the electric capacity versus amount adsorbed. The monolayer generally has a lower dielectric constant than would be expected for the liquid, due to orientation of the molecules on the surface. The second and higher layers may be somewhat more free to respond to the electric field than in the body of the fluid in a small capillary owing to the presence of the free surface, but may be less free than the average molecule in a large capillary not subject to capillary compression. Thus one might expect theoretically to find both "normal" and "inverted" hysteresis loops, and in fact, both are observed.

The rate of surface diffusion of adsorbed molecules under a gradient in spreading pressure has been discussed by Babbitt (91) who argues that the resistance force per unit volume at unit velocity should be nearly constant, independent of the amount adsorbed. Despite earlier reservations, Carman (92, 93) is now also largely persuaded to this view, and cites several supporting experiments including those of Gilliland, Baddour & Russell (94) on flow in porous glass plugs. These latter authors have observed rates of flow for hydrocarbons through microporous Vycor plugs of up to 17 times that predicted for no adsorption. At the molecular level, Takayanagi (95) gives analytical expressions for the scattering cross-section and diffusion coefficient of a two-dimensional adsorbed gas.

Physical interactions.—Studies on the energy of adsorption and lateral interaction have become increasingly sophisticated through the use of homologous series of rare gases and homologous changes of substrate, as well as through the introduction of such new techniques as the field-emission electron microscope. Thus, for example, Gaines & Rutkowski (96) have examined the effect on the adsorption isotherms of argon and krypton of a substitution of the cesium ion for the potassium ion in micas. Gaines' theoretical analysis (97) shows that the isosteric heat of adsorption of argon on the cesium mica averages nearly twice that on the potassium mica, demonstrating the sensitivity to the polarizability of the substrate. The differences in behavior of argon and krypton are discussed in terms of geometrical models, assuming localized adsorption. Martin (98) has measured

the adsorption of water on Li, Na, K, Cs, and Mg kaolinites and traces the observed hysteresis to the hydration of the exchangeable ions. Measurements of the water adsorption on various aminobentonite complexes by Kurilenko & Mikhalyuk (99) demonstrate that the hydrophilic character decreases with increasing size of the organic cation. Still another substrate change is involved in the work of Ross & Pultz (100) who compare the adsorption isotherms of argon on graphitized carbon with those on boron nitride, which also has the graphite structure. Following the treatment of de Boer & Kruyer (101), Ross & Pultz conclude that the theoretical entropies for mobile (van der Waals) adsorption are clearly in much better agreement with experiment than are those for localized adsorption. The two-dimensional condensation temperature as a function of the temperature of graphitization of the carbons is also reported. Nikolaev & Dubinin (102) have compared the adsorption of N_2, Kr, Xe, C_2F_4, and C_3F_6 on two charcoals in the temperature range -195 to $50°C.$, which includes the critical region, and at pressures from 10^{-3} to 700 mm.

In the theoretical treatment that Pierotti & Halsey (74) give their data for the adsorption of Kr on evaporated films of Fe, Cu, and Na, they find that the formula developed by Kirkwood (103) and Muller (104) gives far better agreement with the energy of adsorption than do those of London or Lennard-Jones. This same conclusion was reached by Fisher & McMillan (105) in their studies of the adsorption of N_2, Kr, and CH_4 on the ionic crystal NaBr. Ehrlich & Hudda (55) have made a very detailed field emission study of the absorption of Ar, Kr, and Xe on tungsten, which permits the calculation of the energy of activation for various kinds of surface diffusion and desorption. (For example, the heat of desorption of xenon is given as 8 kcal./mole.) They observe that the binding to the surface is strongly sensitive to the atomic arrangement in the surface plane, being strongest around the 100 pole near the [116] and [130] planes and weakest near the [111] plane, in agreement with calculations based on the dispersion forces. Using similar techniques, Gomer (106) has observed both monolayer and multilayer formation of Ne, Ar, and Kr on tungsten. From desorption experiments, he estimates the heat of adsorption of argon to be 1.9 ± 0.2 kcal./mole into the first layer and $\sim$1.6 kcal./mole into higher layers.

Turning from atoms to molecules, Kington & MacLeod (107) have measured calorimetrically the differential heats of adsorption of N_2, CO, CO_2 and H_2 in natural and calcium chabazites. They conclude that the energetic heterogeneity at low surface coverage does not arise either from the fit of adsorbed molecules into surface cavities or from the variation in dispersion energy between the adsorbed molecule and different types of ion in the solid. Following the suggestion of Drain (108), they find considerable theoretical support for the hypothesis that the heterogeneity arises from adsorbate quadrupole interactions with varying electrostatic field gradients in the solids. Their data incidentally argue in favor of the new chabazite structure proposed by Dent & Smith (109). Papée & Laidler (110) have measured the

calorimetric heat of adsorption of water vapor on sodium chloride and have been able to distinguish the adsorptive stage from the stage in which the water penetrates into the crystal lattice. Papée (111) has extended these measurements to micro crystals of PbI_2, with a view towards elucidating the role of such salt nuclei in cloud-seeding. Drying thermograms of silica gels and activated carbons have been studied by Kazanski (112) and related to the hydrophilic character of the adsorbents. A. V. Kiselev and co-workers (113 to 117) have continued their measurements of differential heats of adsorption of hydrocarbons on silica and graphite.

A particularly interesting observation in the adsorption of nitric oxide on silica has been made by Solbakken & Reyerson (118) who find from measurements of the magnetic susceptibility that the NO is adsorbed below one monolayer in the excited $^2\pi_{3/2}$ state. Evidently in this instance the interaction of the surface with the molecules inverts the order of the doublet energies. The enhancement of the adsorption of large dye molecules on silica gel sensitized by the dye itself has been studied by Morrison et al. (119). Although they find a distinct specificity, they also find that an appreciable amount of the sensitizing dye is permanently retained by the adsorbent. This leads them to question the earlier interpretation of Dickey (120) (lock and key mechanism) in favor of an association mechanism in which the unextractable dye particles act as centers to attract their own kind more strongly than one of their homologs. Such a conclusion, if verified, would have far reaching consequences in molecular biology.

Among the studies of the interactions of physically adsorbed molecules with pre-chemisorbed molecules are those of V. F. Kiselev et al. (121 to 123) who find that the successive dehydration of silica gel affects most strongly the subsequent adsorption of water, somewhat less strongly that of methyl alcohol, and has almost no effect on nitrogen adsorption. That the pore size is also a factor is illustrated by the observation of Belyakova & A. V. Kiselev (124) that a tenfold decrease in the SiO_2 hydration reduced the adsorption of benzene by a factor of 3.5 while at the same time reducing that of C_6H_{14} by only 18 per cent. Sastri and co-workers (125) also have used classical adsorption techniques in investigating the strong and weak chemisorption of CO on supported cobalt catalysts. They find that the retention of chemisorbed CO reduces the amount of nitrogen adsorption subsequently attainable. Klein (126) has observed, in the field-emission microscope at low temperatures, what appears to be a spreading of absorbed CO from multilayers to a monolayer, thus indicating both physical and chemical adsorption. An unusual kind of adsorbate-adsorbate interaction has been observed by Wolff & Hill (127). They find a linear decline in the adsorption of nitrogen or argon on modified carbons with an increasing amount of sodium acetate, aluminum chloride, or sodium hydroxide preadsorbed. With preadsorbed sodium or potassium, however, the adsorption isotherms of both nitrogen and argon go through a sharp maximum that the authors attribute to the formation of new pores. Continuing their examination of the contribution of quadru-

pole moments to adsorbate interactions, Frohnsdorff & Kington (128) have given strong arguments in support of the interpretation of the changes in the OH stretching frequency on silica surfaces in the presence of various physically absorbed gases as due principally to differences in the proton-quadrupole interactions.

Kirchner (129) has related the effect of adsorption on molecular flow of alkali vapors in high vacuum to the mean adsorption residence time. The theoretical steady-state vibrational energy distribution and accommodation coefficients of diatomic molecules temporarily adsorbed from a molecular beam have been obtained by Herman & Rubin (130).

Phase transitions.—Not long ago, transitions in the adsorbed phase had been observed by few and were believed by still fewer. This subject has now come of age however, with East-West agreement: the krypton transition on graphitized carbon observed by Ross & Winkler (131), Amberg, Spencer & Beebe (132), and Clark (133) has been confirmed by A. V. Kiselev & Khrapova (134). These latter authors also observe a transition for methane on the same substrate at a relative pressure of about 0.4 at 78°K. A cautious note is sounded, however, in the work of McDermot & Lawton (135) who find two types of hysteresis for krypton adsorbed on an Acheson GF-3 graphite. The high-pressure hysteresis they ascribe to the usual pore structure, whereas the second type is described as a "swelling hysteresis," and is also observed for SO_2 adsorption (136). In their excellent paper on the interaction of krypton with metals, Pierotti & Halsey (74) showed that the Singleton-Halsey (75) isotherm can be employed in conjunction with theoretical estimates of the adsorption energy to predict with good accuracy the positions of steps in the isotherms. Gomer (106) reports from field-emission observations, that the multilayer films of several rare gases appear to be liquid-like well below the melting point of the bulk adsorbate. A particularly interesting feature is that since all layers but the first act as a dielectric, it is possible to pull the adsorbed phase together on the tungsten point where the field is greatest. These observations also indicate a nucleation of adsorbed "crystallites," which can be "melted" with increasing temperature. It would be interesting indeed if the transitions in a krypton monolayer on a graphitized tip could be witnessed with this instrument.

Graham (137) has given a beautiful example of the effects of surface heterogeneity and changing lateral adsorbate interaction on the appearance of transitions: on the very uniform graphite P-33, both ethane and carbon tetrafluoride show abrupt transitions; but on the slightly less homogeneous surface of graphon, only ethane exhibits a transition, owing to the weaker interaction between carbon tetrafluoride molecules. De Boer & Kruyer (138) have discussed the question of the mobility of physically adsorbed molecules on various surfaces and conclude that mobile adsorption is more likely on charcoal than on salt or oxide surfaces. They emphasize once again the possibly large contribution to the lateral repulsion arising from parallel dipole moments induced in the adsorbate. Shereshefsky & Mazumder (139)

have calculated the entropy of adsorbed krypton on nickel to be about four entropy units less than that expected for the van der Waals' gas. Despite the hindered mobility which this indicates, they go on to apply the two-dimensional van der Waals' equation in the calculation of the induced dipole moment and the two-dimensional transition temperature following de Boer. The dipole moments so calculated are generally greater than one Debye, but appear to correlate well in predictions of the transition temperature when compared with experiment. For example, ethane at 90°K. shows no transition on nickel but does exhibit a transition on nickel oxide. Perhaps one of the most interesting features here is that in the two-dimensional condensed phase the ethane molecules are oriented with the molecular axis normal to the nickel oxide surface in order to take greatest advantage of the enhanced lateral interactions. Such an orientation appears to have been first suggested by Ross (140) in his work on ethane adsorption by NaCl.

From discontinuities in the slopes of the adsorption isosteres for n-butane on various active charcoals, Julis & Hodek (141) have found a phase transition occurring around 250°K with a heat of transition of $\sim$2.5 kcal./mole. Two-dimensional transitions in butane adsorbed on kaolinite and montmorillonite have also been studied by Jurinak & Volman (142). In their work on dimensional changes of Vycor attending adsorption of water, Hodgson & McIntosh (143) have found a remarkable expansion at -22°C., which they suggest may be a consequence of a transition in the adsorbed phase. V. F. Kiselev & Krasil'nikov (144) have even observed distinct steps in the initial portions of the isotherm of phenol adsorbed on silica gel (4.78 μmole/m.^{2}) from heptane solution.

Gas chromatography.—While no general discussion of this rapidly expanding field is possible here, we make note of a few of the more fundamental papers, particularly with respect to isotope separation, and refer the reader to recent monographs (10, 11, 12). Hanlan & Freeman (145) show that the "retention volume" in gas adsorption chromatography is simply related to the "apparent volume" contained in the equation of state for high-temperature physical adsorption derived by Halsey *et al.* (71, 71a, 71b). The application of this theory by Habgood & Hanlan (146) shows that the two parameters of the equation of state suffice to describe a considerable range of chromatographic systems. In particular, the temperature parameter is shown to be simply related to the number of atoms in the carbon skeleton for a series of hydrocarbons. This work appears to provide an important link between the static adsorption measurements and gas adsorption chromatography.

The addition of a second chromatographic column appropriately situated in the flow diagram has enabled Murakami (147) to overcome the previous difficulties encountered in the gas chromatographic analysis of mixtures containing CO_2, and in separating nitrogen and oxygen. Czaplinski & Zielinski (148) have studied the adsorptions of He, Ne, and H_2 on silica gel and alumina at 78°K. and pressures up to 30 atm. At low pressures the adsorption of H_2 is greater than that of Ne which in turn exceeds that of He. Near 30 atm.,

however, the adsorption of H_2 and Ne are nearly equal. They thus recommend pressures in the neighborhood of a few atmospheres for best separation.

The gas chromatography of hydrogen and its isotopes is developing rapidly. Thomas & Smith (149) have obtained a partial resolution of H_2-D_2 mixtures with argon as a carrier gas by the method of gas elution chromatography over palladium deposited on quartz. This problem has also been studied by Kwan and co-workers (150 to 152), who have succeeded in analyzing mixtures of D_2, HD, and H_2. Not only could the mixture be completely separated on the Linde "molecular sieve 5A" used but they were also able to evaluate the equilibrium constant of the reaction $H_2 + D_2 = 2HD$; the value of 3.79 obtained at 300° compares favorably with the theoretical value, 3.69. They have also found that at 78°K. D_2 is strongly adsorbed in comparison with H_2 on the same synthetic zeolite adsorbent. Using this system they have reduced the normal D_2 content in H_2 from 0.0068 per cent to below 0.0005 per cent, thus obtaining substantially pure hydrogen of isotopic mass one.

The separation of hydrogen isotopes by preferential adsorption at 20.4°K. is discussed by White & Haubach (153). An approximate theoretical treatment leads to separation factors for the several possible binary pairs as follows: H_2-D_2(38), D_2-T_2(4.8) and H_2-T_2(188). A measurement on the H_2-D_2 system gave a separation factor in excess of 30. The principal differences in the behavior of the several gases lies in their quantum mechanical zero-point motions. This effect has been examined by Pace & Siebert (154); they measured calorimetrically the heats of adsorption on graphon of p-H_2 and o-D_2 in the neighborhood of their normal boiling points to be 0.910 and 0.950 kcal./mole respectively. Using the Lennard-Jones potential in conjunction with the Kirkwood-Müller formula for the attractive energy, they calculate theoretically a potential minimum of 1.020 kcal./mole and a vibrational force constant of 2400 dyne cm.$^{-1}$, which gives zero-point energies of 0.200 and 0.140 kcal./mole or net adsorption energies of 0.820 and 0.880 kcal./mole respectively, in good agreement with experiment. Basmadjian (155) has measured the adsorption isotherms of H_2 and D_2 both separately and in mixtures at $75 \leq T°K. \leq 90$ and pressures up to one atm. on charcoal, silica gel and three different Linde molecular sieves. Deuterium was adsorbed to a greater extent than hydrogen in all cases, corresponding to an isosteric heat of adsorption greater by 50 to 300 cal./mole. The separation factor was independent of pressure, but varied with adsorbent between the limits of 1.25 to 2.54. In the subsequent thermodynamic analysis, Basmadjian derives an accurate expression for log α that fits his experimental data and is approximated qualitatively by a proportionality to the difference in total vibrational zero-point energy (of adsorbed H_2 and D_2) divided by the absolute temperature. He suggests that the commonly neglected lateral vibrations of the adsorbed molecules may also contribute in an important way.

The effect of hindered rotation in adsorbed hydrogen on the *ortho-para* equilibrium was examined by Sandler (156) using a plane rotator as a model. This problem has recently been re-examined by Evett (157) in a model that permits three-dimensional rotation of the hydrogen molecule but treats each atom as subject to a superimposed parabolic potential due to the interaction with the surface. When fitted at $20°K.$, Evett's theoretical *o-p* separation coefficient is found to agree with the experimental data at $90°K.$ considerably better than Sandler's treatment.

Turning to more complicated systems, Rutz, Graham & Kammermeyer (158) have discussed the role of adsorption in the separation of gases by barrier flow, while Reeds & Kammermeyer (159) have shown that benzene is preferentially adsorbed on porous Vycor from a benzene-methyl alcohol azeotrope vapor. The adsorption of the binary azeotropes of ethyl or methyl alcohols with CCl_4 were reported somewhat earlier by Komarov & Ermolenko (160). An idealized theory of the adsorption-thermal separation of gases having linear and Langmuir isotherms has been formulated by Vagin & Zhukhovitski (161). A numerical solution of the transient stage of isothermal adsorption with nonlinear adsorption isotherms has been attempted by Sugiyama (162). The rate of adsorption from air-vapor mixtures has been treated theoretically by Timofeev (163) for the case where the "inner diffusion" is the rate-limiting process. A similar problem has been attacked by Gol'bert & Alekseeva (164), who determine experimentally the internal diffusion coefficient appropriate to the adsorption of ethylene from hydrogen on cylindrical granules of activated carbon.

CHEMISORPTION

Hydrogen.—Although hydrogen is the simplest chemical substance, our understanding of its chemisorption is still far from complete. Ehrlich (165) has given a detailed theoretical account of some of the most important features, including rates of adsorption, desorption, and surface diffusion, and the distribution and character of the adsorption sites on both metals and non-metals. Unfortunately, very little experimental data is available for comparison, although the situation is improving rapidly. Ehrlich, incidentally, also re-evaluated the heats of formation of various surface hydrides and found these in fair agreement with those calculated from Pauling's geometrical-mean prescription. The bond energies of H and D to the surfaces of Ni, Fe, Pt, and Pd have been calculated by Kiperman & Balandin (166) from the kinetics of *ortho-para* conversion and isotopic exchange. Although these metals have very different catalytic activities, the hydrogen binding energies are very similar. The authors conclude from this that catalytic reaction occurs primarily at active sites that the calculations do not take into account.

Kavtaradze (167) has examined the specific chemisorptive capacity for hydrogen on Ni films and found it practically independent of film thickness. In a subsequent review of the nature of the maxima in the isobars of hydro-

gen chemisorbed on metals, Kavtaradze (168) cites data supporting the view that equilibrium is attained even at low temperatures. In order to account for the observed adsorption he postulates a chemisorption of the H_2 *molecule*, which acquires a positive charge relative to the metal. In the ensuing thermo-dynamic discussion, it is demonstrated that this hypothesis can be made to fit the experimental data, with adsorption enthalpies of 40 to 60 kcal./mole for atomic and 4 to 9 kcal./mole for molecular chemisorption. Clearly, great care is necessary to distinguish the proposed molecular chemisorption from such variants of atomic chemisorption as those described by Mignolet (169) and Hickmott & Ehrlich (170). In any event it should be possible to test this provocative theory directly by a combination of field-emission, spectral, and NMR measurements, as well as magnetic techniques similar to those described by Selwood (171).

Culver and co-workers (172) have measured the change in work function of three *sp* metals (Cu, Ag, Au) and three transition metals (Fe, Co, Ni) at-tending the adsorption of hydrogen or carbon monoxide at $-192°C$. The results, given in Table II, show no evident correlation with either the work

TABLE II

SURFACE POTENTIAL DIFFERENCES (VOLTS) FOR HYDROGEN OR CO ADSORPTION

Metal	Cu	Ag	Au	Fe	Co	Ni
S.P.D., H	−0.35	−0.34	−0.17	−0.43	−0.33	−0.33
S.P.D., CO	+0.30	+0.40	+0.93	−1.68	−1.50	−1.38
1° Ioniz. Pot.	7.22	7.58	9.23	7.83	7.34	7.63
Work function	4.39	4.38	4.8	4.7	4.1	5.0
No. unpaired *d*-electrons in bulk metal	0	0	0	2.2	1.7	0.6

function or the number of unpaired electrons in the bulk metal; but where the first ionization potential of the metallic atom is high (viz., gold), the S.P.D. (surface potential difference) is considerably more positive than for the other elements of the same group. The authors argue that H-chemisorp-tion corresponds to a two-dimensional solid solution where the H-atom takes up the position of greatest symmetry and highest coordination number with respect to surface metal atoms, e.g., in the center of the lattice square and within the actual surface of the metal. The pileup of negative charge around the H-atom gives a negative S.P.D. (i.e., a dipole with its negative pole pointing outward from the metal). From the fact that hydrogen on copper is desorbed at an appreciable rate at $-78°C$. and completely at $-50°C$., a value of ∼8 kcal./mole is obtained for the heat of adsorption, in marked contrast with the value of ∼30 kcal./mole for Fe, Co, and Ni. They suggest that this difference is due to lateral bonding to four surface metal atoms by

overlap of the *dsp* hybrids with the orbital of the H-atom, leading to a bond of considerable strength. The S.P.D. values for CO clearly show the distinction between the two metal classes. The positive values on the *sp* metals indicate that the molecule fits with its oxygen atom towards—and the carbon atom away from—the surface. For the transition metals, the high negative S.P.D. values imply bonding similar in strength and character to that in carbonyls. Perhaps one of the most precise studies of the dipole moment of adsorbed hydrogen is the work of Eisinger (173). Using the most modern ultra-high vacuum techniques, coupled with highly developed electronics, the determination of the photoelectric threshold as a function of the amount of hydrogen adsorbed on Si leads to a dipole moment of 0.15 Debye, which is to be compared with his earlier measurement of 0.18 Debye for hydrogen on tungsten. From a study of the kinetics of the adsorption of hydrogen on Si, Law (174) concludes that there are two types of adsorbed species, and that the energy of activation is a function of the degree of coverage. The integrated rate expression has the form:

$$2N_M = 2.7 \times 10^{17}p_{mm} + 3.5 \times 10^{11}lnt_{min}.$$

where N_M is the number of H_2 "molecules" adsorbed per cm.^{2}.

Suhrmann & Wedler (175) have measured the changes in electric resistance and photoelectric yield in thin evaporated metal films induced by the chemisorption of hydrogen. On Bi the hydrogen adsorption is very weak and is probably molecular. On Ni and Pt there is evidence that hydrogen is adsorbed both as atoms and molecules. In a similar study of the chemisorption of hydrogen on vacuum-deposited Ni films, Suhrmann and co-workers (176) conclude that the hydrogen is adsorbed in three different types of states: (*a*) atomic and negatively polarized; (*b*) atomic and partially dissociated into protons and electrons; and (*c*) molecular and polarized positively. Heiland & Handler (177) find that adsorbed hydrogen may increase either the *n*- or *p*-type conduction of a Ge surface, depending on the surface pretreatment.

Campbell & Thompson (178) have followed simultaneously the rate of arrival of radioactive Hg on evaporated Ni films and the desorption of tritiated hydrogen from these films. It was found that Hg readily displaced H at 20°C. but that the displacement was incomplete in spite of multilayer Hg adsorption. With films covered to less than 50 per cent of their adsorptive capacity, hydrogen corresponding to 7 per cent of that capacity could not be displaced. For fully covered films, 16.5 per cent was retained. On the assumption that the chemisorbed H atoms require an adjacent H atom in order to be desorbed as a hydrogen molecule, one would expect that a random replacement of H by Hg would leave some fraction of the H atoms isolated, and therefore not desorbable. A stochastic calculation by the authors indicates that this is indeed the case, the average amount left isolated being about 6.5 per cent. In a subsequent paper (179), again using radiochemical techniques, these same authors found that Hg poisoned the nickel film

catalyst for the hydrogenation of cyclopropane but not of propylene. The adsorption affinities in descending order are propylene > Hg > H > cyclopropane. The poisoning of the cyclopropane reduction can be explained from the fact that Hg displaces both H and cyclopropane, which therefore cannot come together on the surface. A geometrical study of the configuration of propylene on the Ni surface, however, indicates a considerable van der Waals repulsion between the propylene molecule and Hg atoms adsorbed adjacent to it, whereas H atoms in those same positions would not suffer this repulsion; thus for these sites the affinity of H is greater than that of Hg.

Turning to ionic lattices, an approximate calculation has been made by Tskhai (180) of the bond energies of hydrogen with lattices of the type considered by Vol'kenshtein. The theoretical heat of adsorption is found to diminish with decrease in lattice spacing normal to the surface and to increase with increasing ionization potential of the adsorbate atom M, the residue of which (in the form of the positive ion M^+) becomes part of the lattice. Myasnikov & Karpov (181) similarly attribute the change in conductivity of ZnO-type semiconductors in a hydrogen atmosphere to the change in concentration of the quasi-free electrons resulting from the dissociation of chemisorbed H_2 molecules into atoms and their subsequent ionization into chemisorbed H^+ and conduction electrons.

The rates of hydrogen chemisorption have long been known to follow the Elovich (182) equation. In 1952 Taylor & Thon (183) gave a qualitative explanation for this equation based upon the generation and subsequent disappearance of adsorption sites on exposure to the chemisorbing gas. In their words, this rate equation implies "the rate of slow chemisorption is governed by the availability of sites and, further, that chemisorption eliminates sites over and beyond actual occupancy." Of the two reactants, adsorbent and adsorbate, it is the mass action of the adsorbent sites only that determines the rate at each moment. In two subsequent papers (184, 185) Taylor developed a more quantitative formulation and, with Low, has applied this to numerous experimental systems: H on Ir, (186); H on Ru-Al₂O₃ (187); H on ZnO (188); H on CO preadsorbed on Ru-Al₂O₃ (189); and H on ZnO·Cr₂O₃ (190). The production of new surface sites and the concomitant enhanced hydrogen chemisorption brought about by electrodeless discharge has also been studied by Low & Taylor (191) and by Low (192). Parravano, Friedrick & Boudart (193) have reviewed and repeated some earlier observations on the rates of adsorption of hydrogen and deuterium on a variety of zinc oxides. There proves to be no isotope effect in the rates of adsorption, which fact therefore appears to be good experimental support for the hypothesis that the slow step in this chemisorption process is associated with the spontaneous generation of active centers on solid surface. The Elovich equation has also been found by Matsuda & Nakata (194) to be applicable to the adsorption of hydrogen on Pd films.

Chemisorbed H on the [100] face of a single Ni crystal proved undetectable in the low-energy electron diffraction studies of Farnsworth, Schlier & Tuul

(195). Its presence could be indirectly established, however, from the diffraction of water and nickel hydroxide formed on exposure to O_2. On the basis of x-ray diffraction analysis, James & Straumanis (196) have identified the films formed on Ti, Zr, and Hf in $0.1N$ HF as the corresponding hydrides.

Carbon monoxide.—In their pioneering spectroscopic work on the chemisorption of CO on rhodium, Yang & Garland (197) identified three chemisorbed species: (*a*) two CO's per site (absorption maxima at 2027, 2095 cm.$^{-1}$), (*b*) single linear CO (2040 cm.$^{-1}$), and (*c*) bridged CO (1905 cm.$^{-1}$). A new absorption at 4290 cm.$^{-1}$ has been observed by Pickering & Eckstrom (198) and attributed to the first overtone of physically adsorbed CO, since the band disappears on evacuation of the cell. Their interpretation of the peak at 2060 cm.$^{-1}$ as due to an isolated linear CO attached to a surface rhodium atom may be subject to some uncertainty owing to the coincidence with the average of the frequencies under (*a*) above.

Garland (199) has also studied the infrared spectrum of CO on Ni supported on alumina. Two bands at 2045 and 1910 cm.$^{-1}$ are observed at low coverage and attributed respectively to a CO bonded to a single Ni atom, and bridged between two adjacent Ni atoms. With increasing adsorption two new bands at 2075 and 1960 cm.$^{-1}$ appear and ultimately dominate the spectrum. These Garland attributes to the same respective configurations, with frequencies modified by the interaction of neighboring adsorbed CO molecules. On exposure to CS_2 vapor, the absorption due to the bridged CO structures is eliminated while the band at 2075 cm.$^{-1}$ increases relatively. The CO-Ni system was also examined by Pickering & Eckstrom (198) using a multiple reflection mirror technique. They observed a strong absorption at 4.859 μ, which appears under higher resolution as a doublet with maxima at 4.877 and 4.853 μ, in close correspondence with the two highest frequencies observed by Garland above. Pickering & Eckstrom further note that all absorption disappears upon evacuation, indicating that CO is less strongly adsorbed on Ni than on Rh.

In the adsorption of CO on a tungsten emitter, Klein (126) has observed a monolayer surface migration at $T > 625°K$. having an energy of activation of about 36 kcal./mole. Above 1000°K. desorption occurs with an energy of activation of 52 kcal./mole and is first-order in the area covered. For comparison, the heat of adsorption due to van der Waals' forces lies between 3 and 5 kcal./mole. The chemisorption of CO on tungsten changes the work function from 4.56 to 5.4 ev. There is evidence for the clustering of adsorbed CO molecules at around 600°K., and also for two chemisorbed states having radically different energies of adsorption. Hayward & Gomer (200) note that the chemisorption of CO_2 on tungsten probably occurs as $CO+O$, which would explain the abnormally high heat of adsorption.

Gardner & Petrucci (201) have correlated the absorption spectrum of CO adsorbed on transition metals and alloys with the effective number of valence electrons associated with the CO group. A very regular progression of the frequency with the degree of filling of the 3d band is observed. These

authors also report on the influence of adding oxygen or fluorine to the surface and find that these systems also fit into the regular pattern.

For CO on ZnO, Barry & Brimelow (202) postulate the structures $-C^+ = 0$ below 50°, and CO_2^- above 150°C. At high temperatures CO can be desorbed only as CO_2. With the aid of measurements on the electrical conductivity of ZnO, Keier & Chizhikova (203) have studied the chemisorption and oxidation of CO, and note that the addition of lithium oxide at one atomic per cent Li suppresses the adsorption of CO above room temperature.

Ethylene.—The paper of Pickering & Eckstrom (198) quoted above was principally concerned with the infrared absorption and reaction of ethylene on Rh mirrors. In contact with this catalyst ethylene rapidly generates ethane as the only product identifiable in their infrared spectral range. However, on evacuation of the ethane followed by subsequent addition of hydrogen, more ethane is formed in an amount just half that obtained directly from the initial ethylene reaction. This ratio would be permitted by only one of the four mechanisms considered by the authors and leads them to postulate the existence of C_2 molecules produced on the catalyst surface by the disproportionation of three ethylene molecules into two ethane molecules. It is this adsorbed C_2 that is presumed, on hydrogenation, to give one additional mole of ethane. This elegant work shows the power of the spectroscopic method in this new field.

Formic acid.—The chemisorption and catalytic decomposition of formic acid are inseparable. The several different lines of study, using isotopic and spectral techniques, are providing convincing evidence for the existence of the formate ion as an adsorbed intermediate in the decomposition. Hirota & Otaki (204, 205) have measured the decomposition rates of formic acid and its two possible singly-deuterated derivatives at around 100°C. on reduced silver. From the fact that D_2 is produced from the decomposition of the monodeuterated formic acids even under conditions where the exchange reaction of hydrogen is negligible, it is evident that the decomposition cannot proceed exclusively by a unimolecular mechanism. The composition of the resulting hydrogen-deuterium gas mixture differs for the two monodeuterated acids and also differs from the gaseous equilibrium isotope distribution. On this basis two decomposition mechanisms are proposed, both involving the adsorbed formate ion as an intermediate, one unimolecular and the other bimolecular in formate ion. Block & Kral (206) have made a detailed examination of the isotopic influence on the decomposition rate and have proposed several transition-state models for comparison with experiment. Unfortunately, their deuterated acid samples were not obtained in as high an isotopic purity as those of Hirota & Otaki, nor did they consider the formate ion intermediate. Again on silver, the decomposition rates decrease in the order HCOOH > HCOOD > DCOOH > DCOOD. The dependence of the reaction rate on pressure is little help in deciding the mechanism inasmuch as the rate is zeroth order for pressures greater than about one ton,

presumably due to saturation of the active sites. Of the three transition states examined in detail, the observed isotopic dependence of the rates would appear to favor one in which the carbonyl oxygen is chemisorbed to the metallic surface and the two hydrogens are in the process of leaving. Such a mechanism was apparently first suggested by Eley & Luetic (207). The catalysis and electron-diffraction studies of Sosnovsky, Ogilvie & Gillam (208) on the [111] face of Ag after bombardment with argon ions suggests that the active sites correspond to points where dislocation lines emerge.

Hirota et al. (209 to 211) have examined the near infrared spectrum of adsorbed formic acid and found an absorption characteristic of the metal formate that is present only while the decomposition reaction is in progress. This band at 1580 cm.$^{-1}$ has been found in the decomposition of formic acid on Cu, Ni, Zn, Ag, Pd, Rh, and Pt. This same result has been obtained for Ni supported on silica by Fahrenfort & Hazebroek (212), but does not appear on silica alone (213). A characteristic absorption in the far infrared at 410 cm.$^{-1}$ has also been noted by Hirota & Nakai (214) and attributed to the vibration of the adsorbed formic acid perpendicular to the metallic surface.

Tamaru (215) has studied the formic acid decomposition on Ag, Ni, and Cu in a circulating system which permits following not only the total pressure but also the composition of the gas phase. The results for Ni are very striking. It is observed that hydrogen appears in the gas phase after very little formic acid has been added, but that CO_2 appears only after at least five times as much formic acid has been adsorbed. At this stage the amount of "adsorbed" hydrogen atoms to "adsorbed" CO_2 is unity, which strongly suggests the same formate ion mechanism proposed by Hirota et al. On this basis the increase in resistivity of Ni films on which formic acid decomposition is occurring, as observed by Suhrmann & Wedler (216), can be explained in terms of the electron immobilization brought about by formate ion formation. Ruka, Brockway & Boggs (217) have found no evidence by x-ray diffraction for surface metal formate formation, but it seems unlikely that this technique can rule out the possibility of a monomolecular formate layer. The decomposition of formic acid on filaments at temperatures around 1000° has been examined by Riekert (218).

A correlation between pore size in silica gels and the decomposition path of formic acid at temperatures ~300°C. has been observed by de Pradel & Imelik (219), such that large pores favor dehydrogenation over dehydration. In the same temperature regime, Schwab, Block & Schultze (220) have brought to bear an impressive array of techniques, including conductivity and magnetic susceptibility, to explain their observations on the catalytic enhancement of Ni, Co, and Ag films by small quantities of divalent or tetravalent oxides added to the supporting alumina. For example, some observed activation energies for Ni were: pure Al_2O_3, 20.5 kcal./mole; $Al_2O_3 + 5$ mole per cent NiO, 7.0; $Al_2O_3 + 2$ mole per cent GeO, 23.2. Rienäcker (221) adduces evidence of a correlation of the catalytic activity of alloys and

metallic oxides with the nature of the electron bonds, in support of the theory of Dowden (222). An alternative interpretation of some of Rienäcker's earlier data is offered by Krause (223).

Single crystal studies are becoming increasingly necessary with the experimental refinement and sophistication now possible. A comparative study by Rienäcker (224) of the decomposition rates of formic acid and hydrazine on the [100] and [111] planes of Cu gives virtually the same activation energy for both substances on both faces. However, the decomposition rate is over three times as great for formic acid and only half as great for hydrazine on the [111] as on the [100] face! Other single crystal studies include those on Cu of Crocker & Robertson (225), who find a first-order decomposition of formic acid on the [111], [110], and [100] faces at pressures $\sim 10^{-2}$ mm. The reaction probability is within a few powers of ten of $\exp(-\Delta E\ddagger/RT)$, where the activation energy $\Delta E\ddagger$ is different for each face. Block & Vogl (226) conclude, from a study of $\Delta E\ddagger$ as a function of pressure, that the catalytically active surface of Pt is not substantially heterogeneous. The mechanism of dehydration of formic acid is discussed in terms of a rate-determining impact reaction.

Hydroxyl groups.—In the light of their model of hydrogen bonding between adsorbed polar molecules and surface hydroxyl groups, Folman & Yates (227) have re-examined the observation that water adsorption on silica produces expansion rather than the expected contraction. The present infrared study indicates that at low coverage the water molecules are mainly hydrogen-bonded to each other rather than to the isolated hydroxyl groups on the silica surface. In contrast to this, methyl alcohol apparently is hydrogen-bonded to the surface hydroxyl groups, and thus produces a net contraction of the rigid porous glass upon which the adsorption occurs. In a subsequent article (228) these authors have examined the infrared spectra of adsorbed ammonia, acetone, and methyl chloride. The peak optical density of the perturbed silanol band increases linearly with coverage, but passes through the origin at zero coverage only for methyl chloride.

The spectrum of the silanol group has also been studied by A. V. Kiselev & Lygin (229). At low water content of the silica, only isolated $-$OH groups appear in the infrared spectrum. At increasing coverage a new adsorption associated with hydrogen bonding of adjacent groups appears. When the silanol groups are deuterated by exposure to D_2O the stretching frequency is changed by an amount exactly predicted by the square root of the reduced mass ratio. In a similar study, Benesi & Jones (230) obtain essentially identical results, and identify the absorption bands of the water-silica gel system as given in Table III.

The effect of the bound water on the adsorption of water and alcohols has been studied by V. F. Kiselev and co-workers (231, 232), while A. V. Kiselev & Muttik (233) have examined the hydration of a silica surface by water vapor. The effect of repeated hydration and dehydration of silica has been the subject of two papers by Zhdanov (234, 235) and a comment by

TABLE III

ABSORPTION BANDS OF THE WATER-SILICA GEL SYSTEMS

Maximum (cm.$^{-1}$)	Assignment	Maximum (cm.$^{-1}$)	Assignment
3730 (m)	OH stretching	1640 (w)	SiO overtone
3580 (m)	OH stretching*	1635 (m)	HOH bending
2760 (m)	OD stretching	1430 (m)	HOD bending
2620 (m)	OD stretching*	1200 (sh), 1095 (vs)	SiO stretching
2000 (w)	SiO combination	870 (m)	SiOH bending
1875 (w)	SiO combination	810 (s)	SiO stretching

vs = very strong, s = strong, m = medium, w = weak, sh = shoulder

* hydrogen (or deuterium) bonded, very broad

Sidorov & Nikitin (236). Madeley & Sing (237) give experimental evidence that the adsorption of ethyl alcohol occurs only at special sites on the silica surface, presumably where favorable hydrogen-bonding can occur. The silica gel area and number of such special sites are found to be functions of the pH used in the silica gel preparation. Changes in the pore and surface structure due to high temperature treatment of silica has been discussed by Wolf & Beyer (238). Infrared spectroscopic evidence for a high-solubility layer on the surface of quartz powder (2 to 5μ) has been found by Cignitti & Uva (239). According to Wheatley (240), the solution of SiO_2 and of its easily-soluble surface layer are insignificant factors in silicosis. Slabaugh (241) has determined the adsorption of water on a wide variety of homoionic bentonites, while de Boer & van Doorn (242) have studied the water adsorption and consequent swelling of graphitic oxide.

Eyraud, Lenoir & Corbet (243) consider the surface of Al_2O_3 from the point of view of the Lewis-Brønsted acidity, and give a thermogravimetric method for its determination. Weiss and co-workers (244) have employed their earlier discovery (245), that diborane can replace hydrogen in the silanol groups by boron atoms, to determine the number of hydroxyl groups attached to silicon and to aluminum in silica-alumina catalysts. When silica gel is exposed to diborane at room temperature, approximately three molecules of hydrogen appear for each diborane molecule reacting. With alumina, however, the hydrogen/diborane ratio is almost exactly unity. As an incidental observation that throws light on the mechanism, the reaction of deuterodiborane with surface hydroxyl groups yields only HD. The new observation is that all of the reacted boron on silica can exchange with B^{10} whereas only 50 per cent of the boron reacted with alumina can undergo exchange. A similar result also has been found for pentaborane (246).

Kotov & Terenin have noted that the ultraviolet and visible absorption spectra of adsorbed aromatic amines on alumina-silicates show the presence of acid centers, whereas this surface exhibits electron acceptor properties towards ammonia and methyl cyanide. The present work (247) shows that

the poisoning of the alumina-silicate catalyst by sodium or lithium ion destroys the capacity to donate protons, but leaves unaltered the electron acceptor capability. Roev & Terenin (248) have studied the infrared spectra of water, ethyl alcohol, and methyl alcohol on chromium oxide. With the aid of their measured water spectrum they have demonstrated that even at room temperature both alcohols react to give adsorbed water, hydroxyl groups, and unsaturated hydrocarbons. Hamamura (249) has studied the rate of reaction of water vapor with a hot tungsten filament in the temperature range 1500–2000°C.

Conclusion and acknowledgment.—Limitations of space and time have required that a survey of the vast and complicated subject of catalysis be left to more competent hands in future years. The existence of the recent reviews mentioned in the introduction will compensate in large measure for this omission.

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POLYMER SOLUTIONS[1]

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Introduction

This review is intended, in some degree, as a continuation of that by J. J. Hermans (1) which appeared in this series in 1957. The emphasis has thus been placed on progress made during the years 1957 through 1959; but for the sake of continuity in discussion, many earlier publications have also been cited. Because of the obvious limitation of space nothing like a complete analysis could be attempted of even the restricted field indicated by the title. Indeed, advantage has been taken of this restriction to indulge freely personal inclinations in the selection of material. Prominence is given to studies that relate closely to matters of principle, in preference to those that simply present experimental information, however excellent. Since an adequate appraisal of research on polyelectrolytes would easily constitute another entire review article, the subject is not covered here. Neither are dynamic mechanical phenomena treated although steady state rheological properties are reviewed.

Configuration of Polymer Chains

The question of the excluded volume—i.e., of the deviation of polymer chain statistics from strict random-flight behavior owing to forces exerted between remotely connected chain segments when in close proximity— remains a major problem concerning the configuration of polymer molecules for which a definitive solution has not been found, though much progress has been made within the last decade. For some years Wall and co-workers (2, 3) have been using Monte Carlo methods to calculate average dimensions of model polymer chains with excluded volume. Essentially, the method consists in using a digital computer to generate random walks on some specific type of lattice. A flight is continued step-by-step until an intersection occurs, whereupon the experiment is discontinued and a new one begun. The major handicap of the method lies in rapid attrition of walks, which makes it difficult to obtain sufficiently large samples representing long polymer chains. Wall *et al.* have discussed methods of overcoming the attrition problem by combining already formed short walks (4) and by reduplicating successful walks according to a prearranged scheme before continuing the addition of random single steps (5) to the point where an impossible configuration is reached. For flights of up to 800 steps on a tetrahedral lattice, the mean square end-to-end distance $\langle r_n^2 \rangle$ is given by

$$\langle r_n^2 \rangle = 1.40 n^{1.18}$$

for a chain of n steps each of unit length. It cannot be determined whether in the limit of infinite n the ratio $\langle r_n^2 \rangle / n$ converges, but the power of n

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in the equation cannot be unity for any physically realistic number of steps in the model. Wall & Erpenbeck (6) have extended the Monte Carlo experiments to determine the mean square radius of a polymer chain and the mean square separation between pairs of elements. The mean square radius is found to be proportional to $\langle r_n{}^2 \rangle$ but the proportionality constant is smaller than the value 1/6 given by an unrestricted random flight.

Yamakawa & Kurata (7) have determined certain dimensions of the familiar "string of beads" molecular model—the even moments of the distribution function of the distance between any two segments, the mean square distance between a segment and the center of mass, and the radius of gyration—in the form of the random-flight quantities multiplied by series in powers of the variable

$$z = \beta n^{1/2} (3/2\pi b_0{}^2)^{3/2},$$

β being the mutually excluded volume for a pair of statistical segments separated by links of mean square length $b_0{}^2$ in the random-flight chain of n segments. The results agree with earlier derivations, by somewhat different methods, of Fixman (8) and others; but since the series are slowly convergent and only the first two or three terms can be evaluated, applicability is limited to systems in poor solvents (9) near the characteristic temperature Θ, at which β vanishes and random flight behavior obtains.

For a practically useful theory of chain configuration in good solvents it is necessary to resort to a simplified molecular model yielding a result in closed form, or at least a form amenable to numerical computation. To meet this problem Flory (10) substituted, for the real chain, a distribution of chain segments spherically symmetrical about the molecular center of mass. By a statistical treatment of the spherical model Flory derived an expression of the form

$$\alpha^5 - \alpha^3 = Cz \qquad\qquad 1.$$

for the factor α by which the sphere is expanded beyond random-flight dimensions by the volume effect: i.e., $\alpha^2 = \langle R^2 \rangle / \langle R^2 \rangle_0$ if α is defined in terms of the mean square radius of gyration $\langle R^2 \rangle$, the subscript zero referring to an unperturbed random flight. Recently Casassa & Orofino (11) investigated the effect of certain approximations made in the statistical mechanical calculation on the value of the constant C and showed that any disagreement between the theoretical C and a value deduced from experiment cannot be attributed to the assumption, adopted by Flory, of a Gaussian average segment density distribution instead of the correct (for a random flight) sum of n Gaussians. Grimley (12) also examined the configurational statistics of a spherical model, one obtained by averaging the segment distribution about one end of the chain. Although the form of Equation 1 is obtained by Flory's method with this model, as from any other variety of equivalent sphere, the value of the numerical factor is naturally altered. By another derivation, the details of which are not given, Huggins (13) finds a proportionality of $\alpha^6 - \alpha^4$ to z in place of Equation 1.

These configurational studies concern interactions of remotely connected portions of chains. Local interactions, which may be described in terms of chain stiffness, are simply subsumed into the statistical segment length b_0 to be obtained from an independent theory or by experimental measurements of chain dimensions. Since Eyring, in 1932, proposed a method of calculating the mean square end-to-end distance of a chain as a function of bond lengths, bond angles, and internal rotations, many authors have refined his scheme in various ways to account for hindrances to rotation about the skeletal chain bonds. Of course to be able to use the theoretical expressions in calculating molecular dimensions, one needs some independent information about potential energies for the bond rotations. If a degree of correlation in rotations only about successive bonds in the polymer molecule is assumed, the theory of Markoff chains can be applied in determining average dimensions (14). Gotlib (15) and Birshteĭn (16) have discussed the effect of hindered rotation on the optical anisotropy of polymers. Nagai (17) has calculated the effect of hindered but independent rotations about skeletal bonds on molecular size and the mean square electric moment of isotactic and syndiotactic structures. Lifson (18, 19) has developed a matrix technique for treating the interferences between neighboring R groups in the chain $(-CH_2 \cdot CHR-)_n$ and in particular has derived the mean square end-to-end distance for isotactic and syndiotactic structures with the simplifying assumption that interactions between neighboring methylene groups are unimportant. Ptitsyn & Sharonov (20) have obtained similar results. In a discussion of the polyethylene molecule, Lifson (21) has shown that his theory can be generalized to include orders of interaction beyond first neighbor groups in the chain $(CR_2)_n$. Hoeve (22) has also used the matrix method to account for interaction between any two consecutive rotations in the chains $(-CH_2 \cdot CR_2-)_n$ and $(-CH_2 \cdot CHR-)_n$. Recent work on chain configuration by the active Russian school has been summarized by Vol'kenshteĭn (23).

If a polar chain segment has no dipole moment along the chain contour, the dielectric behavior is independent of the excluded volume effect; i.e., the mean square electric moment of the molecule is proportional to the degree of polymerization. A possibility is thereby afforded (23) for studying short range interactions of polar side groups if the dipole moment of the isolated monomer unit can be inferred from measurements on low molecular weight substances. Marchal *et al.* (24, 25) find that the proportionality to n holds for polymethyl methacrylate in various solvents and further that the short range interactions are independent of solvent.

From the even moments of the segment pair separation, the angular intensity distribution $P(\theta)$ of Rayleigh scattering from a chain composed of point scattering sources with excluded volume can be expressed (7) by the well known $P(\theta)$, obtained by Debye, for a random-flight coil plus a double series of correction terms in powers of z and $\sin^2(\theta/2)$, θ being the scattering angle measured with respect to the direction of the incident light

beam. Necessarily, this series exhibits the same convergence difficulties as appear in the calculation of chain dimensions and therefore is useful only at rather small values of z. Several recent papers give determinations for $P(\theta)$ over the entire angular range. The methods are all based on a model used earlier by Peterlin (26) in which the distribution function for separation r_m of two chain segments linked by m segments along the chain contour is Gaussian but the relation of r_m to the mean square end-to-end distance is

$$\langle r_m^2 \rangle = \langle r_n^2 \rangle (m/n)^{1+\nu}$$

where ν is positive for positive excluded volume. When $\nu = 0$ this model, combined with the general expression for $P(\theta)$, gives Debye's random-flight result, but an exact analytical solution for arbitrary ν has not been found. Hyde $et\ al.$ (27) have determined $P(\theta)$ numerically while Benoit (28) and Ptitsyn (29) have obtained approximate analytical forms by use of incomplete gamma functions. All agree that volume exclusion has a qualitative effect similar to polydispersity in that, for a given initial slope, plots of $P^{-1}(\theta)$ against $\sin^2(\theta/2)$ become progressively more concave downward as ν increases. Hyde $et\ al.$ and Loucheux, Weill & Benoit (30) have analyzed data on very high molecular weight polystyrene. It is evident from their results that measured radii of gyration and molecular weights are seriously in error in good solvents when molecular weights are of the order of 10^6 to 10^7 and calculations are based only, as is commonly the case, on the scattered intensity $R(\theta)$ at 90° and the dissymmetry ratio $R(45°)/R(135°)$ with $P(\theta)$ assumed as that for a random-flight coil. A similar experimental study has been made by Éskin (31).

For some polymers with extremely stiff chains, the freely jointed chain is inadequate for statistical calculations. In such instances there has been used the "worm-like" chain of Kratky & Porod (179) in which the average cosine of the angle between vectors that define successive indefinitely short segments approaches unity. Some time ago Peterlin (32) derived $P(\theta)$ for this model; but since his expression is in the form of a slowly convergent series in powers of $\sin^2(\theta/2)$, Hermans & Hermans (33) have extended the calculations, obtaining $P(\theta)$ by a graphical integration. These last authors have also determined the analytical form for $P(\theta)$ of a random zig-zag chain, a sequence of rods of equal length connected by universal joints. Neither of these models contains an excluded volume effect. The statistics of both approach the random-flight case as the chains become very long, and if in addition the structural details characteristic of each model are of a scale much smaller than the wavelength of light, $P(\theta)$ reduces to that of the random-flight chain of structureless scatterers.

Bigelow & Cragg (34) report a discontinuity (a small but rather sharp maximum or minimum) in the mean square radius measured by light scattering for polystyrene dissolved in a mixture of polyvinyl acetate and a solvent as the concentration of the second polymer is varied. The maximum or minimum corresponds to a similar maximum or minimum (discussed below) found in the intrinsic viscosity of polystyrene in the same systems,

but the concentration at its appearance in light scattering is higher by a factor of about 1.3.

Kilb (35) has discussed the determination of the extent of random branching in heterogeneous polymers containing tetrafunctional crosslinks. Surprisingly, when such polymers have the distribution obtained in a polyester type condensation, the ratio of the z-average $\langle R^2 \rangle$ to M_w is independent of the degree of branching.

THERMODYNAMIC PROPERTIES

The most rigorous treatment of the statistical thermodynamics of polymer solutions has been based on methods developed in connection with the theory of real gases; but because of the enormous complexity of chain statistics, only for the problem of interaction of two solute molecules have even the beginnings of a really satisfactory exact theory been achieved. Results therefore relate only to the second virial coefficient in the equation of state, and hence the theory is generally useful only for rather dilute solutions. In 1946, Zimm (36) began the development of this approach on the basis of the molecular distribution functions used by Mayer, Montroll & McMillan in the general theory of fluids. A number of recent publications have either carried rigorous calculations to a further stage or have used the same formalism in the development of approximate models.

By this method, the virial coefficient is obtained as a series in integral powers of z, the terms relating to probabilities of successively greater numbers of simultaneous contacts between pairs of segments. Unfortunately the difficulties already described in connection with the statistics of single chains are compounded; and although Zimm calculated the term linear in z (corresponding to double intermolecular contacts) the next term has yet to be evaluated completely. Albrecht (37) succeeded in determining the contribution from all intermolecular contacts to this triple contact term while Yamakawa (38) included the effect of some of the configurations with two intermolecular and one intramolecular contact. It is possible, however, that contributions from the neglected triple contact terms are practically negligible. In view of the difficulties attending evaluation of the z^2 term in the series, calculation of higher terms appears remote, even by machine methods (37). Since this series converges slowly, like those expressing the mean dimensions of polymer molecules, its utility is limited to small z.

The severe limitations of the rigorous theory obviously suggest the application of molecular models with spherically symmetrical segment distributions in studies of thermodynamic properties. Using a somewhat more elaborate statistical calculation with a uniform density sphere model employed earlier by Flory (39) and treating thermodynamic interactions as the interpenetration of two such spheres, Emery (40) has calculated the entropy of mixing in athermal systems. The resulting equation of state agrees with Flory's through the second virial coefficient. That higher terms are different seems to be without significance, since in neither theory are interactions of more than two molecules taken into account. The theory

of Flory & Krigbaum (10), in which the second virial coefficient is calculated from the interpenetration of spheres with Gaussian distributions about the centers of mass, has stimulated developments based on other models of similar character. Isihara & Koyama (41), for example, replace the single Gaussian function with the sum of n Gaussians proper for a random flight; and Grimley (12, 42) discusses the statistical thermodynamics of his model with the segment density averaged about one end of the chain. Casassa & Markovitz (43, 44) adopt the device of designating an arbitrarily chosen contact between two molecules as an "initial contact" and then average the segment distributions of both molecules about this point to represent a bimolecular cluster as a single spherical cloud of segments. Mathematically, this last approximation amounts to the assumption that the conditional probability of simultaneous intermolecular contacts, in addition to the first, is given by the product of the independent probabilities of occurrence of each additional contact individually.

The derivations based on the smoothed density models have used the Flory-Huggins lattice treatment in small volume increments shared by segments of two molecules (10) or have adopted the method of molecular distribution functions (12, 41, 44). Equivalent results for the second virial coefficient are found in either way and can be expressed in the form:

$$A_2 = \frac{N_0 \beta n^2}{2M^2} F(z/\alpha^3)$$
2.

i.e., a factor invariant to molecular weight M (N_0 denoting Avogadro's number) multiplied by a complicated function F. The constant factor is simply the virial coefficient in the Flory-Huggins lattice theory. In Flory's (10) symbolism this is:

$$\frac{N_0 \beta n^2}{2M^2} = \frac{\bar{v}^2}{V_1}\psi_1\left(1 - \frac{\Theta}{T}\right) = \frac{\bar{v}^2}{V_1}\left(\frac{1}{2} - \chi_1\right)$$

where $\bar{v}$ is the partial specific volume of polymer, V is the molar volume of solvent, and ψ_1 is an entropy parameter. Qualitatively, F decreases monotonically from unity to zero as z increases from zero; an exact evaluation generally requires numerical or graphical integration.

The theories founded on the two-center models averaged about the molecular centers of mass give quite similar results (45), but the concentric segment distribution of Casassa & Markovitz leads to a much more rapid decrease in F with increasing z. Although the function for the last theory apparently cannot be written in analytical form, the simple expression

$$F(z/\alpha^3) = [1 - \exp(-5.68z\alpha^{-3}]/5.68z\alpha^{-3}$$
3.

deviates from the exact value by less than one per cent for positive z. It is an important advantage of the concentric model that its symmetry facilitates calculation of α for the bimolecular cluster (46), since inclusion of the effects of both intramolecular and intermolecular interactions on α is difficult with a two-center interaction model. Though comparisons with experiment are somewhat ambiguous because of uncertainties in the parameters entering

into z and the constant factor of Equation 2, the observed molecular weight dependence of A_2 appears to be in better agreement with the concentric distribution theory than with the others (44). Casassa (46) determined α by assuming the form of Equation 1 and adjusting C to give the correct dependence of α^2 on z in the limit $z = 0$. Ptitsyn & Éĭzner (47) have found good agreement between experiment and Equation 3 with the effective α determined from an approximate expression for the actually non-Gaussian distribution of segment pair separations within a single polymer chain. Koyama (48) has used a Gaussian density sphere, practically equivalent to the model of Isihara & Koyama (41), and the method of Rushbrooke & Scoins (180) to calculate the radial distribution function, in dilute solution, for separation of molecular centers of mass and thence the second and third virial coefficients. The ratio $A_3/A_2{}^2M$ thus afforded increases from zero at $z = 0$ to a value of 0.704 at $z = \infty$, in very good agreement with an earlier approximate calculation by Stockmayer & Casassa (49). However, since the third coefficient A_3 must contain a contribution from ternary clusters of segments, which does not vanish with β, A_2 and A_3 cannot strictly vanish at the same temperature (50).

Schulz & Craubner (51) combine cryoscopic, osmotic, and light-scattering results of a number of investigators to exhibit the molecular weight dependence of A_2 over a wide range. They find that the form of Equation 2 with the F of Isihara & Koyama appears reasonable for some systems but incompatible with the data for others. The comparisons they draw depend to some extent on the approximation, among others, that α is independent of molecular weight. The A_2 given for the system polystyrene-toluene could not conceivably conform to any of the present theories leading to Equation 2 but does agree with a form of lattice theory developed by Münster (52).

Orofino & Flory (53) have modified the Flory-Krigbaum theory to obtain a function F containing a second dimensionless variable in addition to z/α^3. This is accomplished by the earlier procedure of applying lattice theory in small volume elements containing segments of two molecules; an additional term, the cubic, is retained in the power series in solute concentration expressing the contribution of polymer-solvent interactions to the free energy of mixing. According to the lattice theory then, the chemical potential of solvent in a solution containing a volume fraction v_2 of polymer with molar volume x times that of the solvent would be written, in Flory's notation (10):

$$\mu_1 - \mu_1{}^0 = RT\left[\ln\left(1 - v_2\right) + \left(1 - 1/x\right)v_2 + \chi_1 v_2{}^2 + \chi_2 v_2{}^3\right]. \qquad 4.$$

In a development utilizing the general statistical theory of fluids, an equivalent procedure must involve the abandonment of the approximation that only interactions of segment pairs need be considered, and the introduction of mean potentials explicitly referring to simultaneous interactions among three segments. Such interactions will then be characterized by an excluded volume effect in addition to β for pairwise interactions. If additional terms in the free energy of mixing are required in the theory of the

second virial coefficient, they should also appear in the intramolecular configurational theory. From this point of view the right-hand side of Equation 1 may be regarded as the first term in a series expansion (53) in half-integral powers of the molecular weight.

Orofino and Flory, utilizing osmotic and light scattering data and intrinsic viscosity measurements interpreted by the method of Fox and Flory (10), conclude that the intermolecular and intramolecular theories carried to the new approximation are consistent, and that the introduction of the new parameters markedly reduces the apparent variation of χ_1 (or β) found in measurements covering a very wide molecular weight range. Another important result of the Orofino-Flory theory is the prediction that Θ, now defined as the temperature at which A_2 vanishes, is slightly dependent on molecular weight, at least at low molecular weights. Evidence for this is still equivocal, but McIntyre, O'Mara & Konouck (54) do report a very small effect in the polystyrene-cyclohexane system for polymers prepared without a chain transfer agent. The difficulty of unambiguous interpretation of the data is indicated by the observations of the same authors that if the polymers are prepared with n-butylmercaptan as the chain transfer agent, the Θ (normally found to be 34–35°C.) is much too high, and furthermore exhibits a large dependence on molecular weight (a decrease from 49° to 40° for a molecular weight increase from 22,000 to 115,000). The only apparent explanation for this surprising effect is the presence of sulfhydryl groups at the chain ends.

The dilute solution theories have been discussed here primarily from the point of view of the molecular weight dependence of the second virial coefficient. The thermodynamic and configurational parameters β and b appearing as constants are evaluated independently. The prediction of the temperature dependence of A_2 presents an even more formidable task since, in addition to an acceptable statistical theory, the form of the intermolecular (or more basically, the intersegmental) potential of average force must be known. Isihara & Koyama (55) calculated A_2 for the interaction of uniform density spheres with intermolecular segment pairs interacting according to the Lennard-Jones potential. Koyama (56) then worked out a more elaborate treatment with spheres having the correct random-flight radial distribution of segments about centers of gravity. The most questionable aspect of this approach is, perhaps, the assumption of the unrealistic Lennard-Jones potential for segment interactions which, for example, leads to the prediction of a maximum in A_2 as in simple gases. Another defect, though not one essential to the theory, is the assumption that α is constant rather than a function of z.

It its original form, the celebrated lattice theory of Flory & Huggins marked the most notable single advance in the understanding of the large deviations from Raoult's law exhibited by polymer solutions. It fails, however, in two important respects: first, the second virial coefficient is predicted to be independent of molecular weight; and second, even though the simple form of the theory (Equation 4 with χ_1 independent of concen-

tration and $\chi_2 = 0$) may agree fairly well with experiment for some systems, the enthalpy and entropy contributions to χ_1 usually vary individually with v_2. Historically, the smoothed density spherical models were introduced as a remedy for the first defect, which arises from the neglect in the lattice model of the fact that a very dilute polymer solution must be discontinuous in structure; the domains of dissolved chain molecules being separated, on the average, by regions of polymer-free solvent (10). Since this objection does not apply to concentrated solutions, the cause of the second difficulty is to be sought in configurational properties of the polymer molecules and nonrandom mixing that results from free energy differences between polymer-polymer and polymer-solvent contacts. Recently, Huggins (13, 57) has refined the enthalpy and entropy calculations to account for these effects and obtains a linear relation between the two contributions to χ_1. This behavior is actually observed in the rubber-benzene system, which gives a χ_1 nearly concentration independent, but the linear relation has also been found to hold in some cases in which a single χ parameter must be taken as concentration dependent (58, 59). Kilb & Bueche (60) and Krause (61) have discussed extension of the lattice treatment to solutions of a graft copolymer, and Danon *et al.* (62) have considered the relationship between degree of grafting and polymer solubility.

Among recent studies of concentrated polymer solutions, the careful investigation of the polystyrene-cyclohexane system by Krigbaum & Geymer (63) is of particular interest since they combined osmometry, isopiestic equilibration, and vapor-pressure lowering to obtain solvent activity for the entire concentration range at the theta point and at temperatures ten degrees higher and lower. Their osmotic measurements, at polymer concentrations up to about 0.25 gm. cm.$^{-3}$, demonstrate that some of the higher virial coefficients are positive when the second is zero or even negative. Thus a clear indication is given of the inadequacy of a theory in which all interactions are characterized by the excluded volume β, since the vanishing of segment interactions implies the vanishing of molecular interactions of all orders. Krigbaum & Geymer did find that in the concentration range accessible by osmometry, Equation 4 with $\chi_1 = \frac{1}{2}$, $\chi_2 = \frac{1}{3}$, fits the data at Θ (it also follows from the expansion of the logarithm in Equation 4 that A_2 and A_3 are then both zero); at higher concentrations more χ parameters are needed. Rehage & Meys (59) studying the same system by osmometry over about the same concentration range were also able to fit data with two χ parameters, but the temperature dependence of their constants leads to a value of Θ much too low and to A_3 negative when A_2 vanishes. Krigbaum and Geymer found a single van Laar term inadequate to express the partial molar heat of dilution: i.e., $\Delta \overline{H}_1 / \overline{R} v_2^2$ increased slowly and linearly with v_2 up to $v_2 = 0.4$ and very rapidly thereafter, exhibiting a type of behavior reported also in other systems (64, 65).

Flory & Daoust (66) also have employed osmometry to study relatively concentrated solutions of polyisobutylene in cyclohexane and in benzene at several temperatures. At the theta temperature in benzene, two χ parameters

are adequate to fit the data but A_3 is found to be positive when A_2 vanishes. This work and other recent studies (64, 67 to 69) provide rather extensive activity data for the polyisobutylene-benzene system.

Maron (70) has recently outlined a new theory of the thermodynamic properties of polymer solutions. In his derivation the free energy of mixing is expressed by means of Hildebrand's "free volume" formalism with the addition of contributions, written in the usual van Laar form, due to interactions between components. The theory is thus equivalent to the simple form of the Flory-Huggins lattice treatment (10) except in allowing for volume changes upon mixing; but the novel (and controversial) feature lies in the introduction of an effective solute volume ϵv_2, with the factor ϵ, generally a function of v_2, determined from viscosity measurements as interpreted by Maron and collaborators (cf. below).

The question of phase equilibrium in polymer solutions has been reviewed recently by Voorn (71). Experimental studies of particular systems and applications to polymer fractionation techniques continue to appear in fair numbers; but little theoretical development has been reported beyond the familiar treatment (10) based on the Flory-Huggins lattice theory. Broda *et al.* (72, 73) have considered the problem of molecular weight distributions obtained in precipitation of polymer fractions, but their results depend on approximations of the lattice theory. Stockmayer (50) has discussed the relation of the phase separation problem to rigorous dilute solution theories for A_2 and A_3 in connection with determination of ψ_1 and Θ by Flory's method (10) from the molecular weight dependence of the critical miscibility temperature. The value of ψ_1 obtained in this way, unlike that for Θ, is dependent on a special Flory-Huggins value $\bar{v}^2/3V_1$ (corresponding to $\chi_2 = 0$) for the third virial coefficient. This approximation may partially account for the difficulty that the value of ψ_1 obtained from phase separation studies usually does not agree with that deduced from the temperature dependence of A_2 near Θ. An illustration is the system polyisobutylene-benzene (66) mentioned above.

Since Rayleigh scattering from dissolved polymers at finite concentrations is determined by correlations in position of all pairs of scattering elements, intramolecular and intermolecular, a complete theory must combine, together with the electromagnetic calculation, all the apparatus of the treatment of the configurational statistics of single chains and of the orders of molecular clusters. Realization of such a theory therefore faces the obstacles already discussed. In the treatment of Zimm (74), which is exact to the approximation of single contacts between two polymer molecules, the virial equation of state relative to light scattering is found to be

$$\frac{Kc}{R(\theta)} = \frac{1}{MP(\theta)} + 2A_2c + \cdots \qquad\qquad 5.$$

with the coefficient of the linear term independent of the scattering angle θ. Using Zimm's method, Albrecht (75) has carried the rigorous calculation

one step further, including bimolecular clusters with double contacts, to obtain in place of Equation 5 the expression

$$\frac{Kc}{R(\theta)} = \frac{1}{MP(\theta)} + 2A_2 Q(\theta)c + \cdots$$

in which the function $Q(\theta)$ is unity at $\theta = 0$. Since Albrecht obtains $Q(\theta)$ explicitly only as a double series expansion in powers of z and $\sin^2(\theta/2)$ evaluated through but two terms, applications are generally limited to small scattering angles and solutions for which $F(z/\alpha^3)$ is near unity. Qualitatively, however, the indicated decrease in $Q(\theta)$ with increasing angle is observed experimentally.

Applying the Flory-Krigbaum model in machine calculations, Flory & Bueche (76) have determined $R(\theta)$ at large values of z and θ, obtaining results also in accord qualitatively with experiment. In their derivation the model is invoked in accounting for intermolecular interference; but the intramolecular scattering factor is taken as $P(\theta)$ for the random coil since the smoothed density model, which ignores the connectivity of the polymer chain, cannot correctly give interference in scattering between pairs of segments within a single molecule. This theory too agrees qualitatively with experiment in that $Q(\theta)$ is a decreasing function of the angle, and consequently the slopes of the concentration lines on the conventional Zimm plot (74) decrease with increasing angle.

By using the appropriate grand canonical ensemble and expressing composition fluctuations in solution in terms of volume, temperature, chemical potentials of solvents (designated arbitrarily), and concentrations of solutes, as independent variables, Ooi (77) has calculated the turbidity of a multicomponent system composed of particles that are small compared to the wavelength of light (so that $P(\theta)$ is unity). The result is, of course, equivalent to the more familiar one based on fluctuations, at constant temperature and pressure, of volume and concentrations relative to a fixed mass of one component. However, the refractive index increments appearing in the equations are specified differently: in the first case with volume, temperature, and chemical potentials of solvent components held constant, and in the latter with pressure, temperature, and concentrations fixed.

Although the ultracentrifuge has long been used successfully in studies of protein solutions, adequate theoretical treatment of random-coil polymers has proved to be a forbiddingly complex problem. In principle, the sedimentation equilibrium method is an extremely powerful one, capable of yielding molecular weights, molecular weight distributions, and thermodynamic information. However, the combined effects of the redistribution of the ordinarily heterogeneous polymer in the centrifugal field and of the very large deviations from thermodynamic ideality in good solvents make interpretation of data extremely difficult. A fairly straightforward analysis is possible if solutions sufficiently dilute to obey van't Hoff's law can be used; but limitations on the refractive index difference between solution and sol-

vent, imposed by the refractometric optical systems ordinarily employed in determining concentrations and concentration gradients, frequently make this impossible. The recent introduction, commercially, of much more sensitive interference optics should, however, make it feasible to work at considerably lower concentrations. Instead of attempting to approach ideality by dilution of polymer in a good solvent, Mandelkern, Williams & Weissberg (78) made measurements at the theta temperature (on polyisobutylene in ethyl n-heptanoate) and concluded that reliable molecular weights could be obtained in this way irrespective of heterogeneity. Fujita (79) has published a method of analysis of equilibrium data applicable to a polydisperse polymer at such concentrations that deviations from van't Hoff's law are linear in concentration (i.e., that the second virial coefficient adequately characterizes the equation of state). Another experimental problem in centrifugation is the long time ordinarily required for attainment of sedimentation equilibrium. Since the transient period is proportional to the square of the height of the column of solution, even a modest shortening of the column would effect a substantial saving in time. Van Holde & Baldwin (80) have obtained fairly accurate molecular weights in columns as short as one millimeter. The time required can also be shortened by starting with a step distribution of concentration set up in a synthetic boundary cell (81).

The Archibald principle offers yet another way of avoiding lengthy equilibrium experiments. At sedimentation equilibrium there is no net transport of any solution component through any level in the column. This condition, as Archibald (82) observed, necessarily applies at either end of the column at any time; hence a knowledge of concentration and concentration gradient at either of these points is equivalent to knowledge of the same quantities at any position after attainment of equilibrium (if the solute is homogeneous). Kegeles, Klainer & Salem (83) have demonstrated that the Archibald technique can be used to measure weight average molecular weights in polydisperse nonideal systems. The interpretation of data is not complicated by polydispersity since measurements are made before redistribution of solute in the centrifugal field occurs; and extrapolation of results to infinite dilution to obtain the correct molecular weight appears practical. Erlander & Foster (84) have shown experimentally that both weight average and z-average molecular weights in paucidisperse systems can be obtained from Archibald experiments.

The theoretical aspects of ultracentrifugation have recently been reviewed comprehensively by Williams *et al.* (85).

Although in principle the theory of osmotic pressure has been understood for decades, the idealized situation is not always realized in practice; and some empirical anomalies have still to be completely resolved. Patat (86) has contributed a summary of the present status of knowledge concerning the various membrane effects which make it difficult to attain true osmotic equilibrium, and Elias *et al.* (87, 88) have studied the behavior of certain membranes. The familiar difficulty of permeability of a membrane to low molecular weight polymers makes of obvious interest the question of the observable osmotic pressure due to a diffusible solute not at equilibrium.

Some time ago Staverman applied the methods of irreversible thermodynamics to this problem; and more recently Staverman, Pals & Kruissink (89) discussed the theory in connection with measurements made using a membrane permeable to about one-third of a heterogeneous polystyrene sample. The experiments showed qualitative agreement with the theoretical prediction that the apparent osmotic pressure, the applied pressure at which net volume flow vanishes, is always less than the true osmotic pressure and falls with time; hence the common procedure of empirical extrapolation to zero time does not lead to the correct osmotic pressure (nor therefore to the correct molecular weight). To a first approximation, measurements at very long time should lead to the correct osmotic pressure of nondiffusible components, but in fact the measured pressures were found much too low, even after solute permeation had been accounted for. The only likely explanation was failure to reach complete equilibrium. Other workers (90 to 92) also observed that the osmotic pressure due to a diffusible solute is too low. Gardon & Mason (91) showed that after an initial period the logarithm of the apparent osmotic pressure becomes nearly linear with time. Extrapolation from this region back to zero time gives a value from which, in combination with independent dialysis and diffusion experiments, the correct osmotic pressure can be calculated. Tung (93) has examined the problem from a kinetic point of view to estimate the magnitude of error involved in apparent osmotic pressures extrapolated to zero time.

Donnet, Roth & Meyerhoff (94) found the osmotic second virial coefficient for polystyrene in toluene to be higher for unfractionated polymer than for fractions of the same number average molecular weight and surmised that the effect was due to loss of low molecular weight material through the membrane. The Flory-Krigbaum theory, however, predicts that the virial coefficient may indeed be increased by heterogeneity; and the prediction is supported by experimental data on mixtures of two sharp fractions of greatly differing molecular weight (95, 96).

RHEOLOGICAL PROPERTIES

Since the flow characteristics of polymer solutions are intimately related to the configurational properties of the macromolecules, the question of the excluded volume must arise in rheological problems. The most direct link with the nonequilibrium properties is through the theory of the molecular friction constant f. For dilute solutions, at the limit of high molecular weight in which hydrodynamic shielding causes a dissolved polymer molecule and enclosed solvent to move as a unit, the theory of Kirkwood & Riseman (97) gives for a chain of n segments in a medium of viscosity η_0:

$$f = 6\pi\eta_0 R_s, \qquad R_s^{-1} = n^{-2} \sum_i \sum_{i \neq j} \langle r_{ij}^{-1} \rangle$$

where $\langle r_{ij}^{-1} \rangle$ is the mean reciprocal separation of segments i and j. Using the perturbation technique developed by Fixman (8), Stockmayer & Albrecht (98) obtained two terms in an exact series expansion for the equivalent Stokes law radius R_s

$$\alpha_s = R_s/R_{s0} = 1 + 0.609z + \cdots$$

in which R_{s0} is the random-flight value of R_s. Attacking the same problem independently, Yamakawa & Kurata (99) obtained a coefficient 0.417 in the second term by an approximate calculation. In either case α_s varies less rapidly with z, at least near the temperature Θ, than does α, which is

$$1 + 67z/105 + \cdots.$$

Since at sufficiently high molecular weight the intrinsic viscosity $[\eta]$ is given by

$$[\eta] = \Phi' \langle R^2 \rangle_0^{3/2} \alpha_s^3 / M \qquad 6.$$

according to the theory of Kirkwood and Riseman, it follows that the familiar Flory-Fox treatment, in which α_s is identified with α, should lead to an apparent decrease in the constant Φ' with increasing z or, alternatively, a viscosity varying as a power of α less than 3. The calculations of Yamakawa & Kurata lead to a factor $\alpha^{2.43}$ in Equation 6, and Kurata & Yamakawa (100) found such a dependence actually to be exhibited in data of Krigbaum & Carpenter (101) on the temperature dependence of the intrinsic viscosity of polystyrene in cyclohexane near the theta point. On the other hand, the more exact result of Stockmayer & Albrecht gives a dependence on $\alpha^{2.73}$ (102). Similar theoretical results have also been published by Ptitsyn & Ĕĭzner (103).

Equation 6 represents a general form obtained from any theory in which the polymer molecule is represented by an equivalent hydrodynamic sphere or a spherical cloud of segments essentially impermeable to solvent. The various theories developed in the course of the last 10 to 15 years differ mainly in the value assigned to the constant Φ', i.e., in the determination of the effective radius R_s. The predictions of the theories and comparisons with available experiments are the matter of a recent discussion by Peterlin (104). With decreasing molecular weight, the dissolved chains become progressively more permeable to the flow of solvent and the constant must be replaced by a complicated function of η_0, chain dimensions, and the friction constant of the statistical chain segment. Although 'the asymptotic behavior is realized at rather low molecular weight (less than 50,000) for most polymers, there are stiff chain structures for which Φ' does not assume the limiting value even at very high molecular weights, as in the by now classic instance of cellulose derivatives. Among recent studies illustrative of quasi-permeable behavior may be mentioned that of Meyerhoff (105), who investigated sedimentation, diffusion, and viscosity, for cellulose nitrate in acetone. Flory, Spurr & Carpenter (106) also studied cellulose acetate and trinitrate by viscometry. They found large negative temperature coefficients of $[\eta]$, which they attributed to changes in chain flexibility, and a considerable variation of the characteristic ratio $\langle R^2 \rangle_0/M$ in various solvents, an effect not observed with most other polymers but presumably due to changes in chain conformation caused by specific interactions with solvent. These phenomena could not be explained by inconstancy of Φ'. Moore & Brown (107) reported similar results for solutions of ethyl cellulose.

Erpenbeck & Kirkwood (108) have reformulated Kirkwood's theory of

irreversible processes in polymer solutions to include additional perturbations of solvent flow and have applied the results to a discussion of the intrinsic viscosity problem. In a new treatment of the hydrodynamic behavior of branched polymers, Zimm & Kilb (109) have essentially repeated the work of Kirkwood and Riseman on straight chains except for use of a normal coordinate treatment and inclusion of hydrodynamic interactions between chain segments. They conclude, for several models in which branches radiate from a single branch point, that the ratio of the intrinsic viscosity of a branched molecule to that of a linear molecule of the same weight varies almost with the square root of the ratio of the mean square radii instead of the 3/2 power as supposed earlier.

The derivations of the intrinsic viscosity referred to above do not include non-Newtonian behavior since they either relate to the limit of zero shear or give a viscosity independent of rate of shear. Using a system of coordinates rotating with a random-flight chain model possessing some stiffness, Takemura (110) has solved the appropriate diffusion equation in approximation to obtain a steady shear viscosity which decreases with increasing shear rate. Such an effect, in qualitative agreement with experiment, is also given by theories of Bueche (111) and Pao (112). These theories all predict that the ratio of $[\eta]$ to its value $[\eta]_0$ at zero shear rate is a universal function of the product of shear gradient and $M\eta_0[\eta]_0/RT$. Although none of the functions predicted is experimentally verified, the fact that the only property of the polymer that appears is the molecular weight has led Bueche & Harding (113) to suggest that comparison of an empirically established master curve with viscosity data can serve as the basis of a molecular weight determination. Comparisons with viscosity molecular weights for polystyrene and polymethyl methacrylate substantiate this proposal, at least qualitatively. It seems clear though, from other experimental studies by Čopič (114) and Golub (115), that such a simple functional dependence for non-Newtonian viscosity effects cannot be generally valid (116, 117). Furthermore, Cerf (118) holds that the non-Newtonian viscosity appearing in all these theories is spurious and arises only because of approximations made at some stage in the derivation. The more exact treatments by Rouse (119) and Zimm (120) of a similar model exhibit no dependence of viscosity on shear rate.

In a number of publications, Cerf (116, 117, 121 to 124) has developed a hydrodynamic theory based on the "Gaussian subchain" model, in which the polymer molecule is represented by a series of subchains, each Gaussian, with the frictional forces acting only upon the junction points. The model is not new, having been discussed in 1948 by Peterlin and by Kargin & Slonimskiĭ (181), and is the basis of the work of Rouse and Zimm; but Cerf has modified it by including an "internal viscosity," a frictional resistance to the relative motion of subchain junctions. This refinement introduces a non-Newtonian viscosity effect. A rather stringent test is possible since the theory permits calculation of $[\eta]/[\eta]_0$ from flow birefringence data without adjustable parameters. A comparison with viscosity measure-

ments on high molecular weight polystyrene shows semiquantitative agreement for gradients up to 20,000 sec.$^{-1}$.

A more rigorous treatment of the mutual perturbation of polymer and solvent motion to include the anisotropy in polymer configuration induced by shearing also leads to a non-Newtonian viscosity [cf. Čopič (125), Peterlin & Čopič (126), and Ikeda (127)]. However, the various approximations required in the calculation make the magnitude of the effect uncertain; in addition, it has not been possible thus far to account for the results of flow birefringence experiments without invoking an internal viscosity (116, 117).

Studying polyisobutylene solutions in capillary viscometers, Brodnyan, Gaskins & Philippoff (128) observed a second Newtonian viscosity at very high shear rate. Merrill (129) carried out more extensive experiments in a Couette arrangement at shear rates up to 100,000 sec.$^{-1}$ and found the ultimate Newtonian viscosity to give the same specific viscosity-concentration ratio η_{sp}/c, independent of concentration and proportional to $M^{1/2}$, in both a good and a poor solvent. According to Crane & Schiffer (130) solutions of polyisobutylene in tetrahydronaphthalene exhibit antithixotropy; i.e., viscosity increases reversibly with shearing stress, but attainment of equilibrium is not instantaneous. While such behavior is unprecedented for solutions of uncharged polymers, it has been recognized before in polyelectrolytes.

It has been known for some years that when polymer solutions are subjected to shear, stresses appear not only in the direction of shear, as in classical fluids, but also normal to the shear surfaces. Markovitz (131) has classified various phenomenological theories of deformation according to the relations among the stress components. On this basis experimental observations on polyisobutylene solutions in three different experimental situations —shearing between parallel plates in relative rotation, between a cone and plate (132), and between coaxial cylinders—have been compared (131) to eliminate certain classes of theories as invalid. In a contribution to the general theory of fluids, Coleman & Noll (133) have established correspondence principles consistent with, but more general than, the results of Markovitz, which make it possible to predict, from the empirical results of a single type of experiment, complete stress and velocity profiles for most of the classical flow problems. Tamura, Kurata & Kotaka (134) find, from measurements of normal stresses in solutions of polystyrene and cellulose derivatives, that the customary superposition procedures used to reduce dynamic mechanial data to a form independent of concentration and temperature are valid for continuous shear only over limited ranges of the variables.

Maron and co-workers (135, 136) interpreted the flow properties of synthetic rubber lattices in terms of a theory of Ree & Eyring (137) according to which the viscosity of a fluid system is a sum of contributions from different "flow units," each type being characterized by a particular relaxation time. Although the physical nature of the flow units is not specified in the theory, the data on lattices at all but the lowest rates of shear could be fitted by ex-

pressions containing two such units having parameters that suggest identification with the spherical latex particles and the aqueous medium. Maron, Nakajima & Krieger (138), studying a single polystyrene sample in a number of solvents at several temperatures, found that up to 20 per cent concentration the viscosity conformed to the Ree-Eyring theory with inclusion of two flow units. From the empirical parameters of the theory, they concluded that the effective hydrodynamic volume of the polymer chains is independent of solvent at concentrations above 4 per cent, and interpreted this to mean that above this limit the polymer chains are coiled into relatively tight masses without intermolecular chain entanglements.

The question of the existence of an anomaly in η_{sp}/c measured in capillary viscometers at very low concentration has continued to be controversial. Though discordant earlier measurements exist, since publication of the work of Streeter & Boyer (139) it has been generally agreed that the experimental phenomenon to be explained is a large increase in η_{sp}/c with decreasing concentration, usually at such low concentration that experimental errors may render ordinary measurements questionable. In a detailed study of polystyrene in toluene, polyvinyl acetate in toluene, and nitrocellulose in ethyl acetate, carried out with the aim of reducing the uncertainty due to each recognized source of error to 0.001 per cent, Öhrn (140) concluded that the effect was due to adsorption of polymer in the capillary and consequent narrowing of the cross-section. In addition, he found some evidence for a sudden decrease in η_{sp}/c at concentrations much lower than the supposed "critical" concentration for occurrence of the increase. On the other hand, Tuijnman & Hermans (141), also studying polyvinyl acetate in toluene, attributed the anomalous effect primarily to non-Newtonian behavior although the absolute value of η_{sp} was affected by adsorption. Hirai (142) likewise proposed explanation of the behavior of η_{sp}/c as a purely viscous phenomenon. Huque, Fishman & Goring (143) in a study of cellulose trinitrate in acetone and in ethyl acetate found the effect explicable by adsorption; and by invoking Öhrn's theoretical analysis concluded that the adsorbed polymer layer was of the order of 500 to 100 A in thickness. Rinsing did not desorb the polymer since the efflux time of solvent was increased after the capillary viscometer had been used for polymer solution.

Kawai & Saito (144) have predicted the existence of a minimum in η_{sp}/c by combining the Flory-Fox relation

$$[\eta] = KM^{1/2}\alpha^3$$

with the Huggins equation

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c$$

and letting the expansion factor α increase with dilution according to a theory of Krigbaum (145). Qualitatively, this kind of dependence of α upon concentration would be expected from the simple consideration that α is greater than unity in a good solvent but equal to unity in undiluted amorphous polymer. Krigbaum's theory may be criticized, however, as involving

the assumption that the expansion of a polymer molecule occurs in a homogeneous dispersion of the segments of all the other polymer chains, an approximation of unknown effect but clearly unrealistic in dilute solutions.

Cragg & Bigelow (146) have reported another kind of viscosity anomaly. Measuring the intrinsic viscosity of polystyrene in a mixture of a solvent and polymethyl methacrylate they found a discontinuity to occur in the curve given by plotting results against concentration of the methacrylate "solvent" polymer. The effect was usually small, and was neither observed invariably nor reproducible in magnitude; but when it was observed it always appeared at the same concentration for the same polymer samples. This critical concentration could be identified crudely as that required to fill the solution volume by simple cubic packing with spheres of radius equal to the root mean square end-to-end distance of the polymer chains. In a further investigation, the same authors (147) concluded that the discontinuity generally appears as a dip if the solvent is a good one for the solute polymer, but as a peak if the solvent is poor. If the solvent is good for the "solvent" polymer, the effect is small or absent.

Sharples & Major (148) consider that heterogeneous polymers of known molecular weight distribution are preferable in establishing the dependence of $[\eta]$ on molecular weight to fractions of unknown sharpness, for which the approximation of equating number, weight, and viscosity average molecular weights may be unacceptable. They suggest preparation of a molecular weight series by subjecting a high molecular weight sample to a random degradation process and interpretation of the viscosity data through use of the geometrical distribution which must at least be approached in the samples upon sufficiently extensive degradation. Onyon (149) and Frisch & Lundberg (150) propose that comparison of viscosity molecular weights M_v in both a good and a poor solvent be used to establish an index of polydispersity. This is a possibility since the exponent a in the Mark-Houwink equation

$$[\eta] = KM_v{}^a$$

appears in the definition of the viscosity average molecular weight

$$M_v = \left(\sum_i M_i{}^a w_i \right)^{1/a}$$

but as a varies only from 0.5 to about 0.8 from a very poor to a very good solvent the criterion is a rather insensitive one.

As in the case of equilibrium ultracentrifugation, sedimentation velocity measurements have proved exceedingly valuable in studying monodisperse or paucidisperse systems of biological interest; but the typical continuous molecular weight distribution of synthetic polymers and the difficulty of approximating thermodynamically ideal behavior have made difficult the interpretation of measurements on these materials. Cantow (151) has found it possible, however, to determine molecular weight distributions for polystyrene in cyclohexane by working at the theta temperature where the concentration dependence of the sedimentation constant s and the diffusion

constant D is found experimentally to be very small—although it is the first derivative of s/D with respect to concentration which theoretically should vanish at Θ (10). Thus an uncertain extrapolation to infinite dilution (152) can be avoided. Schlieren curves are integrated graphically to give the concentration at each point in the centrifuge cell. Data taken over a period of time are then used in an extrapolation to infinite time to eliminate the effect of diffusion relative to sedimentation. The resulting distribution of sedimentation constants can then be converted to a distribution of molecular weights by use of a relation between s and M. This is best obtained from measurements of s and D for polymer fractions; but at Θ, s is very nearly proportional to $M^{\frac{1}{2}}$ for usable concentrations. Since the analysis involves some approximations as well as graphical integration and extrapolation, one might be inclined to doubt the reliability of results except for the fact that agreement with molecular weight distributions obtained from careful fractionation is excellent. McCormick (153) has reported equivalent results from an almost identical investigation.

The theory of flow birefringence in polymer solutions under shear concerns two problems: form anisotropy, the effect of orientation of deformed polymer molecules in a medium of different refractive index; and intrinsic anisotropy, a manifestation of the internal optical anisotropy of chain segments. In experimental measurements two quantities are obtained, the total birefringence and the extinction angle of crossed polarizers. In former years the interpretation of the extinction angle seems to have received most attention, but in recent theories the birefringence appears more prominently. The form effect is the subject of a theoretical treatment by Čopič (154) who finds, in agreement with observation, a parabolic dependence of form birefringence on the refractive index of the solvent. The theory also predicts a change in sign of the birefringence, first observed by Frisman (155), with variation in shear gradient if the positive form birefringence, that always predominates at low shear rate, is counteracted at higher gradients by a negative intrinsic birefringence. Tsvetkov & Frisman (156, 157), in an independent theoretical development, obtain results in most respects similar to those of Čopič and also discuss the differences in the theories and deviations from experimental observations. Janeschitz-Kriegl (158) has been able to separate the contributions of intrinsic and form anisotropy by measuring the concentration dependence of the birefringence in solvents of differing refractive index. In an effort to test the idea of the internal viscosity, discussed above, Cerf (118, 122) and Leray (159) have dwelt on the dependence of the extinction angle upon rate of shear and solvent viscosity.

Since light scattering yields information about molecular size and shape rather more directly than does flow birefringence, it would be of great interest to compare the two types of data for solutions subjected to shear stress. Although no experimental work of this nature has been reported, Peterlin, Heller & Nakagaki (160 to 162) have calculated the angular distribution of scattering for random-flight chains in a shear gradient. A similar analysis can of course be applied to anisotropic systems produced in other ways, a homo-

geneous electric field, for example, in the case of polar molecules (163). Streaming dichroism, another optical manifestation of anisotropy, has been discussed by Bird (164).

Properties of Certain Polymers

The most thoroughgoing investigations of polymer solutions have involved correlation of information obtained by both thermodynamic and rheological measurements (10). Recent findings from such studies on some polymers of particular interest are indicated briefly in this section.

The synthesis of stereoregular polymers, in addition to being an achievement of great technological importance, has obvious significance in providing new classes of materials for study of thermodynamic and configurational properties. Consequently, work that at least initiates the systematic comparison of stereoregular with random, or atactic, polymers is now being published. Results of such studies may have very wide implications since evidence has been found (165) that some degree of stereoregular placement can occur in ordinary free radical polymerization.

The initial report of Peaker (166) that an isotactic polystyrene dissolved in toluene exhibited no significant difference from normal polymer either in the second virial coefficient or the mean square molecular radius as found by light scattering can be regarded as inconclusive on the ground that the single sample studied was not adequately characterized. Studying the same system, but using a series of fractions, Danusso & Moraglio (167) and Trossarelli, Campi & Saini (168) decided that the relation of intrinsic viscosity to molecular weight is the same for isotactic and atactic polymers but that the second virial coefficient is smaller for the isotactic material. In conformity with this last observation, they found the isotactic polymer to be less soluble than the atactic at the same molecular weight. Krigbaum, Carpenter & Newman (169) agree with the observations of Danusso & Moraglio but conclude that the configurational similarity of the two varieties of polystyrene implied by the viscosity measurements holds only in thermodynamically good solvents. By combining viscosity data and second virial coefficients they deduced that in a theta solvent the atactic polymer has a larger mean square radius. An interesting difference among the last three studies is the much lower solubility of the polymers of Krigbaum et al. with the evident implication of a greater degree of stereoregularity in their fractions. Intrinsic viscosity relations reported by Ang & Mark (170, 171) are in accord with the results of the other workers cited.

Danusso & Moraglio (172), studying various solvent systems, have found little difference in the viscometric behavior of isotactic and atactic polypropylene. The work of Kinsinger (173) and Kinsinger & Wessling (174) on this polymer supports the view of Krigbaum et al. that isotactic and atactic polymers are different configurationally in poor solvents. Kinsinger & Wessling have observed Θ in phenyl ether to be eight degrees higher for the isotactic polymer. The curves expressing virial coefficients as functions of

molecular weight cross, so that at some critical molecular weight the precipitation order is reversed. The same effect appears in the data of Danusso & Moraglio for polystyrene.

Solution studies of polyethylene have been largely motivated by interest in information concerning molecular weight, molecular weight distribution, and occurrence of chain branching. Available information with regard to heterogeneity is somewhat discordant; Raman & Hermans (175) find no grossly abnormal distribution for either high or low pressure polyethylene, but others, Trementozzi (176) for example, present evidence for M_w/M_n ratios as high as 100. Such disagreements are perhaps not surprising when it is considered that problems of experimental technique are severe at the elevated temperatures required for solution studies and that commercial samples may well be variable with respect to such factors as chain branching and the presence of traces of gel-like material removable only with great difficulty.

Chinai and collaborators (177, 178) have investigated a series of fractionated methacrylate polymers by light scattering and viscometry. Comparing the radii of gyration measured by light scattering in theta solvents near room temperature, they find that the ratio of $\langle R^2 \rangle_0$ to the degree of polymerization for the methacrylates studied falls curiously in the order n-hexyl $> n$-octyl $>$ methyl $>$ ethyl $> n$-butyl. Combined with the intrinsic viscosity data, the results for $\langle R^2 \rangle$ do not lead to a constant Φ' independent of polymer and solvent. The two papers cited also give second virial coefficients in butanone, a good solvent. Since these values of A_2 were calculated from scattering at right angles alone (thus with the assumption of Equation 5), they decrease too rapidly with increasing molecular weight and furthermore appear to depend on the wavelength of light used.

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PHOTOSYNTHESIS[1,2,3]

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Several thousand papers on photosynthesis have been published since the subject was last reviewed in this series some seven years ago (1). The topics discussed are obviously somewhat dependent upon the interests of the authors, although we have attempted to emphasize research areas representing the newest approaches, both experimental and theoretical, to the complex and still poorly understood process of photosynthesis. For those unfamiliar with the field, we recommend the small monograph by Hill & Whittingham (2) for a brief, lucid, and authoritative introduction. Details of the older work may be found in the monumental monograph of Rabinowitch, now completely published in three volumes (3). Two major conferences on photosynthesis have been held in the United States in recent years; fortunately the proceedings of both have been published (4, 5). An all-union conference was held in Russia in 1957; abstracts of the papers presented are available in English translation (6). To save space, we have listed only the more recent papers in a series, or, if possible, an appropriate review. These may be referred to for more detailed lists of references.

Since this review will appear in a publication directed largely to physical and theoretical chemists, the authors felt that it might be useful to summarize briefly the biological-biochemical basis of photosynthesis to permit a better integration of the recent developments. The higher plants and algae have the unique ability to absorb light energy by means of a special pigment, chlorophyll, and use it to drive the following reaction

$$CO_2 + 2H_2O \xrightarrow{\text{light}} (CH_2O) + H_2O + O_2 \qquad 1.$$
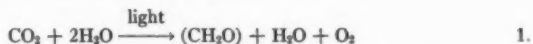
where (CH_2O) represents organic products with the approximate average composition of carbohydrate. The molecular oxygen evolved is apparently

[3] The following abbreviations will be used: CMU [3-(4-chlorophenyl)-1,1-dimethylurea]; DCMU [3-(3,4-dichlorophenyl)-1,1-dimethylurea]; DPN (diphosphopyridine nucleotide); FAD (flavin-adenine denucleotide); FMN (riboflavin phosphate); PGA (3-phosphoglyceric acid); PSP (photosynthetic phosphorylation); TPNH (triphosphopyridine nucleotide, reduced form).

derived entirely from water, while the oxygen of the water produced originates from carbon dioxide. The complex reaction sequences by which carbon dioxide is reduced to organic compounds have been worked out in moderate detail, largely by Calvin, Benson, Bassham and co-workers (7, 8). The photochemical metabolism of photosynthetic bacteria differs from the above in that water cannot be used as a hydrogen source. Instead, such materials as molecular hydrogen, hydrogen sulfide, hydrogen selenide, alcohols, organic acids, etc. are required, depending on the bacterial strain and the growth conditions.

Although physical scientists occasionally neglect the problem, mechanism can only rarely be divorced from structure in biological material. This is especially true in considerations of photosynthesis. Chlorophyll is not distributed at random in plant cells, but is localized in specialized structures termed chloroplasts. In leaves, one typically finds in each cell a number of disc-shaped chloroplasts a few microns in diameter, while in some algae there may be only a single chloroplast per cell. Chloroplasts always contain carotenoids. Red and/or blue chromoproteins, termed phycoerythrins and phycocyanins, are also present in some species of algae. Light energy absorbed by these accessory pigments can be transferred to chlorophyll and used for photosynthesis in some plants. Although several different chlorophylls occur in the higher plants and algae, chlorophyll-a is always present. The photosynthetic pigments in bacteria occur in very small particulate structures termed chromatophores, which appear to be hollow spheres a few hundred A in diameter.

Cells are extremely complex structures. One experimental approach in studying the function of specific cellular components is to break the cells open and isolate quantities of the particular sub-cellular component of interest. This technique has been extensively used in studies of photosynthesis since Hill (9), some 20 years ago, found that isolated chloroplasts would split water when illuminated, with the evolution of molecular oxygen. This reaction, now generally termed the Hill reaction, requires an appropriate electron acceptor (oxidant) such as ferricyanide or quinone and proceeds as follows:

$$2 H_2O + 4 \text{ ferricyanide} \xrightarrow{\text{light}} O_2 + 4 H^+ + 4 \text{ ferrocyanide} \qquad 2.$$

$$2 H_2O + 2 \text{ quinone} \xrightarrow{\text{light}} O_2 + 2 \text{ hydroquinone} \qquad 3.$$
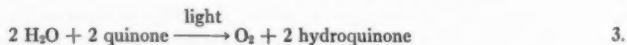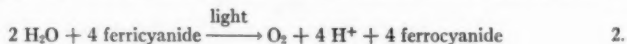
Various physiological electron acceptors can also be used.

More recently, in what is probably the most significant advance in our knowledge of photosynthesis since the last review in this series, Arnon and co-workers, using isolated chloroplasts, and Frenkel, working with chromatophores, discovered a new reaction termed "cyclic" photosynthetic phosphorylation. This reaction proceeds as follows:

$$ADP + \text{phosphate} \xrightarrow{\text{light}} ATP \qquad 4.$$
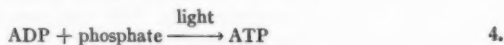
The reaction requires magnesium ion and catalytic amounts of some redox cofactor such as phenazine methosulfate, K vitamins, FMN, etc. Chloroplasts also carry out another reaction, "noncyclic" photosynthetic phosphorylation, which may be summarized as follows:

$$2 \text{ TPN} + 2 \text{ H}_2\text{O} + 2 \text{ ADP} + 2 \text{ phosphate} \xrightarrow{\text{light}} 2 \text{ TPNH} + 2 \text{ H}^+ + \text{O}_2 + 2 \text{ ATP} \quad 5.$$
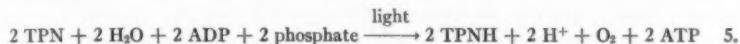
The great importance of these reactions is that they probably provide the necessary energy-rich cofactor, ATP, for driving the carbon dioxide reducing reactions of photosynthesis; the reduction of one molecule of carbon dioxide appears to require three molecules of ATP and two molecules of TPNH (8).

One aspect of photosynthesis exciting great current interest is its possible use in food production and oxygen regeneration in manned space flight. Sufficient food and oxygen could be carried along for short flights; for prolonged flights a closed ecological system balancing man against green plants will be required by payload limitations. In this application algae would probably be more efficient than higher plants, but the problems of growing algae on human wastes, utilizing them as food, developing zero gravity photosynthetic gas exchangers, etc. are complex (10). The engineering problems concerned with putting man into space are much nearer solution than are the biological problems of keeping him alive once there.

Recent advances in rocketry have stimulated new interest in the possibilities of life on other planets. It is probable that other planetary biologies, if they exist, are also based on photosynthetic organisms of some sort. The seasonal waves of darkening that progress from the polar regions of Mars may result from plant growth, for example. The dark areas on Mars have characteristic absorption bands at 3.43, 3.56, and 3.67 μ. The first two bands are very similar to those of organic compounds, probably carbohydrates, characteristic of plants. The third band seemed anomalous at first, however, some terrestrial algae were recently found to show this band (11).

ENERGY TRANSFER AND UTILIZATION

The first step in the photosynthetic process is the absorption of a light quantum by some appropriate photosynthetic pigment such as chlorophyll-a. The excited chlorophyll molecule may then (a) undergo internal conversion to a longer-lived excited state, (b) transfer its energy to an unexcited chlorophyll molecule, (c) lose its energy through a chemical reaction, (d) return to the ground state with the production of heat, or (e) lose its energy through fluorescence. Some of the current ideas on mechanisms of energy transfer and utilization in the photosynthetic process will be presented in this section.

Energy transfer and the photosynthetic unit.—The best documented picture of the photochemical part of photosynthesis suggests that electronic excitation energy migrates from chlorophyll molecule to chlorophyll molecule, and finally arrives at a specialized region of the chloroplast, the "trapping center"

where it is "converted," that is, transferred from the photochemical system to the biochemical system. It appears that several hundred chlorophyll molecules are associated with and transfer energy to the same trapping center thus forming a statistical entity, the "photosynthetic unit" (3). In principle, energy could migrate in the form of a diffusing high-energy compound; however, there is no evidence for such a mechanism. Some photosynthetic schemes do not require energy migration (12), but these are not generally accepted. The transfer of energy from one photosynthetic pigment to another has been clearly demonstrated [see (13)] by observing the excitation of fluorescence with light absorbed by pigments other than the fluorescing pigment. The transfer of energy from one chlorophyll-*a* molecule to another within the chloroplast is more difficult to demonstrate. Arnold & Meek (14) found a marked depolarization of chlorophyll fluorescence in *Chlorella*. This could best be interpreted by assuming that excitation energy was transferred through several chlorophyll molecules before fluorescence occurred. Similar results were obtained with phycobilin fluorescence (15). For details on energy transfer between chlorophyll molecules *in vivo*, the following references should also be consulted (16, 17, 18).

The most generally accepted theory for the movement of excitation energy in the chloroplast is the resonance migration theory of Förster (19), especially as applied to photosynthetic systems by Duysens (13). It is possible, of course, that energy could be transferred in the triplet state, since Terenin and co-workers (20) have demonstrated the excitation in this state. Since the triplet state of chlorophyll-*a* was not detected *in vivo* (21), Livingston & Pugh (22) concluded that only chlorophyll-*a* situated at some unique site is converted from the singlet into the triplet state. They further concluded that concentration quenching cannot be of great importance *in vivo* since, if it were, the fluorescence yield would be one-fifth the observed value [cf. (23)].

The nature of the trapping center required in all schemes involving the cooperation of any sizable number of pigment molecules is largely a matter of speculation. One postulated trapping center involves chlorophyll itself. According to Franck (24), the trapping center consists of a fraction of the chlorophyll, which is modified by the nature of its environment in such a way as to form the energy sink. The pigment giving the absorption change at 700 mμ observed by Kok (25) is an attractive possibility as the trapping center. Little is known of the mechanisms by which excitation energy is converted into some more or less chemically stable form at the trapping center. One possibility is that the conversion involves the photochemical reduction of chlorophyll [the Krasnovsky reaction (26)], since Coleman & Rabinowitch (27) find that reduced chlorophyll may accumulate in illuminated *Chlorella* in concentrations up to 0.3 per cent. In this connection, Marcus & Moss (28) have made the interesting observation that chlorophyll illuminated in organic solvents can reduce menadione to the hydroquinone. The photochemistry of chlorophyll has been reviewed in detail recently by Rosenberg (29). Franck

(30) has postulated that the naturally-occurring oxidant is reduced by the hydrogen atom at carbon 10 of chlorophyll. Some support for this idea comes from the report of Vishniac & Rose (31) that hydrogen is transferred from water to chlorophyll upon the illumination of algae, chloroplast fragments, and acetone powders of chloroplasts. Lumry & Spikes (32) have recently presented a rather detailed discussion of possibilities with reference to the nature and function of the trapping center.

Fluorescence studies.—A knowledge of the fluorescence yield and the lifetimes of the excited states of chlorophyll permits establishing the number of energy transfers possible before dissipation. The nature of the fluorescence behavior also provides information concerning the state of the chlorophyll molecules in the plant structure. Latimer *et al.* (23), by using improved techniques and making better corrections for the absorption of fluorescence both within the cell and externally, find the fluorescence yield of chlorophyll in *Chlorella* to be as high as 3.5 per cent, a value some ten times greater than that previously accepted (3). On extrapolation to zero light intensity the yield decreased to approximately 2 per cent. On the basis of these data, Rabinowitch (18, 33) estimates that up to a thousand energy transfers can take place. The possible number of collector molecules that may be associated with one trapping center is thus increased. Brugger (34) has examined the effects of reaction variables on the fluorescence vs. light intensity relationship of *Chlorella*.

Brody & Rabinowitch (35) and Dmitrievskii *et al.* (36) have examined the lifetime of chlorophyll fluorescence *in vivo* and in a number of organic solvents. In the case of *Elodea* the fluorescence lifetime increased with increasing light intensity (36). When the fluorescence of chlorophyll-*a* in the red alga *Porphyridium* is excited by illuminating phycoerythrin, there is a delay of 0.5×10^{-9} sec. in the onset of fluorescence (35). This agrees with the efficiency of the energy transfer from phycoerythrin to chlorophyll-*a* as reported by Duysens (13). On the basis of discrepancies between measured and calculated fluorescence yields, Brody & Rabinowitch (35) suggested that chlorophyll-*a* occurred in two forms in plants, one non-fluorescent and the other showing a high fluorescence yield. French (37) and Brown & French (38) have presented good spectral evidence for the presence of two or more forms of chlorophyll-*a* in some plants. Studies of fluorescence spectra also support this observation [cf. (39)]. Brody (40) observed a new fluorescence band in concentrated solutions of chlorophyll-*a* and in *Chlorella*, which he suggested might result from chlorophyll aggregation. From studies of fluorescence during the induction period of quinone-treated *Chlorella*, Lavorel (41) tentatively concluded that there are three forms of chlorophyll in cells, and that interconversion of these forms produced the observed induction changes in fluorescence. Mayne (42) and Lumry, Mayne & Spikes (43) have examined the relative fluorescence yield of isolated chloroplasts as a function of light intensity, temperature, and the concentration of Hill oxidants. Parallel measurements on Hill reaction rates demonstrated a simple direct relationship

between fluorescence yield and Hill reaction rate as a function of light intensity; this will be discussed later in the section on the Hill reaction. In summary then, new measurements, especially those involving derivative spectrophotometry (37, 38), stress the complexity of the pigmentation of photosynthetic structures.

The two-light effect (Emerson effect).—One of the most important developments in the study of energy-transfer mechanisms in photosynthesis during recent years has been the re-examination and extension of the original observation of Emerson & Lewis (44) that in *Chlorella* photosynthesis the quantum yield decreased on the long-wavelength side of the red absorption peak of chlorophyll-*a*. This decline is observed in the photosynthesis of a wide variety of organisms [see (45)] as well as in the Hill reaction [see (46)]. The most exciting new finding was that the quantum yield in the long-wavelength region could be increased by supplemental illumination with light of a shorter wavelength [Emerson and co-workers (45; 47 to 50)]. This phenomenon appears to be quite different from the supplementary effects of very low intensities of blue light reported by Warburg *et al.* (51). Lowering the temperature has a similar effect. This "two-light effect" appears to be related to the "chromatic transients" observed by Blinks [see (52) for references] who found transients in oxygen evolution on changing the wavelength, even when the steady state was the same at the two wavelengths used.

Myers (53), in collaboration with C. S. French, has shown that the chromatic transients and the two-light effect have a common origin and that the synergistic effect of light of two wavelengths is still demonstrable even when they are separated in time up to 15 sec. This time interval is of comparable length to those observed by Allen & Franck (54) and Whittingham & Brown (55) in studies of photosynthesis using short flashes of light. The evidence indicates that the two-light effect results from an interaction between the energy absorbed by chlorophyll-*a* and that absorbed by chlorophyll-*b* or some other pigment such as the phycobilins in the red and blue-green algae. Emerson & Chalmers (56) have reported, for example, that algae which contain only chlorophyll-*a* do not show supplementary light effects. More recently, Highkin (57) found that whereas normal barley plants showed the two-light effect, a barley mutant lacking chlorophyll-*b* did not.

Franck (24) interprets the Emerson two-light effect in terms of his "two quantum" theory of photosynthesis. In this proposed mechanism, light absorbed by chlorophyll-*a* produces mainly metastable (lowest triplet state) chlorophyll-*a*, while the short-wavelength light produces singlet excited chlorophyll. The excitation energy from this latter state is then used to excite a chlorophyll-*a* molecule in the metastable state to the first excited triplet level which then drives the photosynthetic reaction. Lumry & Spikes (32) have rcently presented a formal mechanism for the steady-state Hill reaction which includes a simple double-excitation mechanism. On the basis of changes in the absorption at 700 mμ produced by red and far-red irradiation, Kok (25) has proposed a mechanism to explain the two-light effect. Red light

caused an increase in the absorption at 700 mμ while far-red light caused a decrease. Kok suggested that the 700 mμ pigment, rather than chlorophyll-*a*, is the final energy sink in photosynthesis and that it can be formed only through the mediation of chlorophyll-*b*. Light absorbed by chlorophyll-*a* causes a bleaching of this pigment.

Solid state phenomena and photosynthesis.—One of the most active fields of investigation since the last review has been the study of photosynthesis as a solid state phenomenon. Katz (58), a number of years ago, proposed that the photosynthetic pigments functioned as two-dimensional photo-conductive crystals, and that the migrations of holes and electrons, produced on illumination, provided the necessary redox materials to drive photosynthesis. Tollin and co-workers (59) have extensively re-examined the phenomenon of delayed light emission by plants as discovered by Strehler & Arnold (60). Tollin & Calvin (61) concluded that the decay of luminescence of chloroplasts did not result from a simple reversal of any one step in photosynthesis. They suggested that the light produced by photosynthetic material resulted from the recombination of electrons and holes, and that the complicated decay pattern was due to the differences in the energy barriers which the trapped electrons must surmount. In this paper they concluded that the light had its origin in the triplet to ground state transition of chlorophyll. Later (62), however, agreement was reported with Arnold & Davidson (63) that the light originated in the transition from the first singlet excited state of chlorophyll to ground. Tollin *et al.* (64) examined the temperature dependence and quantum yield of luminescence of spinach chloroplasts, *Chlorella* and *Scendesmus*. The integrated quantum yield of luminescence was reported to be of the order of 10^{-6} for *Chlorella* and *Scendesmus* and 10^{-7} for spinach chloroplasts. The quantum yield measurements of *Chlorella* agree with those reported by Strehler & Arnold (60). Tollin *et al.* (64) found appreciable light emission even at $-170°C$. At this temperature the decay showed two components, a fast one that they suggested was related to the charge-carrier lifetime and a slower one related to the freeing of trapped electrons. The time-constant of the slower process (0.03 sec.) is in agreement with the Emerson & Arnold (65) dark-time obtained from flashing-light studies, and the decay time of 5150 A absorption spectra changes in *Chlorella* (66). Because of this agreement in decay time, Tollin *et al.* (64) suggested that the Emerson & Arnold dark time was due to some physical process, perhaps the same one involved in the slow decay of luminescence at $-170°C$. Calvin and co-workers (59, 67) have strongly supported the concept that chlorophyll molecule aggregates in the grana behave as photoconductive and semiconductive crystals permitting conduction bands in which photoproduced electrons and positive holes could migrate. Such a mechanism could permit a separation of the photoproducts in space, which as Rabinowitch (18) has often stressed, is one way that could prevent energy-wasting recombinations. The mechanisms proposed by Calvin and co-workers would involve the photoproduction of unpaired electrons. Commoner and co-workers (68), using

paramagnetic resonance absorption techniques, were the first to actually observe the production of unpaired electrons in illuminated spinach chloroplasts and a chlorophyll-lipoprotein complex. They further observed the production of two kinds of unpaired electron spins; they suggested that one kind, a fast component, represented photochemical reactions, while the other, a slow component, was related to dark reactions. Calvin and co-workers (69, 70) have confirmed these results with observations on the growth and decay of the paramagnetic resonance absorption in illuminated leaves, dried chloroplasts, wet chloroplasts, and "large" and "small" chloroplast fragments at temperatures between 60° and −140°C. The cooling to −140°C. did not greatly increase the time necessary (of the order of seconds) for the growth of the absorption to its maximum value, but did lengthen the decay time after illumination from approximately 30 sec. to hours. In the photosynthetic bacterium *Rhodospirillum rubrum*, the paramagnetic resonance absorption decays rapidly, even at −160°C. (71). Tollin *et al.* (59) suggested that the luminescence of illuminated photosynthetic tissue results from the decay of unpaired electron spins. Oddly, on the basis of preliminary measurements (72), the action spectrum of the photoinduced electron spin resonance signal in chloroplasts did not correspond to the absorption spectrum of chlorophyll, but was shifted toward the red.

In another very interesting approach to photosynthesis as a solid state phenomenon, Arnold & Sherwood (73) showed that dried chloroplasts were thermoluminescent, i.e., if a dried chloroplast film was illuminated and then heated, the chloroplasts emitted light. If the sample was cooled and reheated no luminescence occurred, but if the chloroplast sample was reilluminated, it again showed thermoluminescence. The glow curves were similar to those found with inorganic crystals. When the electrical resistance of dried chloroplast films was measured as a function of temperature, an enormous decrease in resistance was observed as the temperature increased. Again, this is a property of semiconductors. Arnold & Sherwood have recently examined chloroplast glow curves in more detail (74). The curves are complex, in that at least five different activation energies are observed. However, on the basis of experiments to date, they could not decide whether the energy stored in illuminated chloroplasts was in the form of trapped electrons as would be the case for crystals, or whether it represented the formation in light of some high energy chemical compound. Arnold & Maclay (75) have shown that dried films of chloroplasts are photoconductive. They also confirmed earlier observations (76) that thin films of chlorophyll, including monolayers, are photoconductive. Carotene was photoconductive only in blue light; however, the inclusion of small amounts of chlorophyll in the film sensitized it to red light. Illumination of chlorophyll-carotene junctions resulted in a charge separation with the chlorophyll becoming negative. Arnold & Maclay concluded that these experiments suggested, but did not prove, that photosynthetic structures, on illumination, behave like the *n-p* junctions in "solar batteries."

Another possibility as the source of the paramagnetic resonance absorption spectra changes in illuminated photosynthetic tissue is the formation of free radicals. Uri (77) has demonstrated the presence of free radicals in photosynthesizing *Chlorella* by means of methyl methacrylate polymerization. He was unable to detect free radicals during the Hill reaction, but did not consider this sufficient evidence to rule out their participation since some types of free radicals do not initiate polymerization. Using the polymerization of acrylonitrile and the reaction of hydroxyl radicals with benzene as tests for free radicals, Wessels (78) likewise was unable to detect the formation of free radicals during the course of the Hill reaction. Levitt (79) has recently reported more data on his photoelectric theory of photosynthesis.

Kasha (17) has pointed out some difficulties in the application of solid state terminology and reasoning to the study of photosynthesis, while Lumry & Spikes (32) have discussed some of the arguments against the participation of solid state phenomena as major factors in photosynthesis. At present it is probably safest to say, on the basis of the work described above, that photosynthetic structures definitely exhibit solid state properties; it is not clear, however, to just what extent these phenomena are involved in the main line sequences of photosynthetic reactions.

STRUCTURE AND FUNCTION OF PHOTOSYNTHETIC ORGANELLES

The photosynthetic pigments occur in specialized structures, the chloroplasts of the higher plants and most algae, and the chromatophores of the photosynthetic bacteria. These photosynthetic organelles, although complex structures, are still simpler than whole cells. Thus, since they can carry out such processes as the Hill reaction, photosynthetic phosphorylation and carbon dioxide fixation, their study in isolated form has represented one of the major approaches to the elucidation of the photosynthetic process in recent years.

Chloroplast and chromatophore structure.—Considerable information on the fine structure of photosynthetic organelles has become available since the last review, largely as a result of improved electron microscope techniques coupled with better measurements of the chemical composition and optical properties of the organelles. In the space available we can only indicate in brief outline the advances in this very important area. Fortunately there are a number of excellent recent summary and review papers including those of Wolken (80, 81), Hodge (82), Sager (83), von Wettstein (84), and Thomas (85) on the higher plants, and Frenkel (86) and Bergeron (87) on the photosynthetic bacteria.

The chloroplasts of most plants fall into one of two structural categories, the "lamellar" type characteristic of most algae, and the "grana" type represented by the chloroplasts of the leaves of higher plants. There are some exceptions to this general observation. In the lamellar chloroplast, the layers extend uniformly throughout the length and width of the chloroplast. Presumably the chlorophyll and other pigments are distributed over

each lamellae. In the grana-containing chloroplast the layers extend throughout the chloroplast, however, as seen in osmic acid "stained" sections, well-defined regions of the lamellae will have denser walls; these regions line up in "stacks" in mature chloroplasts and result in the structural units termed grana. Dense osmic acid staining is believed to occur in regions of high lipoid content; further, on the basis of light microscope studies and observations of fluorescence, it appears that chlorophyll is confined to the grana. Fragmented chloroplasts are often referred to in the literature as "grana preparations" or "green grana preparations." Most workers present little evidence that such preparations consist entirely or even largely of grana free from stroma material. On the contrary, with some plants, these preparations appear to be composed of random fragments. For example, Park and co-workers (88) recently compared the chlorophyll/nitrogen ratios of different size-fractions from sonically-ruptured spinach chloroplasts. The ratios were found to be rather similar in all fractions, whereas if a fraction were actually rich in grana, a high chlorophyll/nitrogen ratio would be expected. Chlorophyll may well play a structural as well as photochemical role since it appears that both in algae (89) and in higher plants (82) lamellae do not appear unless chlorophyll is present.

A number of similar molecular level structural models have been proposed for chloroplast lamellae including those of Wolken (80, 81), Hodge and co-workers (90), von Wettstein (84), and others [see (80) for references]. These models are based on the thickness and spacings of the lamellar substructures as determined from electron microscope studies, from the measured pigment concentrations, from the dimensions of the pigment molecules, and from various optical measurements; it should be emphasized that available experimental techniques do not permit defining unequivocally the location of various types of molecules in the lamellae. It is generally assumed (80), following the suggestions of Frey-Wyssling, that each lamella consists of a lipoid-pigment or lipoprotein-pigment layer intimately in contact with and separated by aqueous protein layers; the chlorophyll is assumed to occur as monomolecular layers with the lipophilic phytol groups inserted into the lipoid layers and the more hydrophilic porphyrin groups associated with the aqueous protein layers. The total lamellar surface available in the chloroplast just provides space for a monolayer of the chlorophyll porphyrin heads present. Goedheer (15) on the basis of a detailed study of the dichroism, birefringence, and polarization of chlorophyll in chloroplasts and *in vitro* concluded that the chlorophyll molecules were in monolayers. The porphyrin heads were oriented parallel to the lamellae, although the orientation was relatively poor (which would account for the rather weak dichroism of chloroplasts). The low value for the polarization of fluorescence in chloroplasts found by Arnold & Meek (14) also indicates a low degree of order in the chlorophyll molecules. Goedheer suggested that the poor orientation could be accounted for if the porphyrin planes were in proximity to the spherical macromolecules that apparently compose the lamellae. Calvin

(67) and others have pointed out that weak dichroism would also result if the chlorophyll molecules were tilted in alternate directions in the different layers. Jacobs *et al.* (91) on the basis of *in vitro* studies with crystalline and amorphous chlorophyll monolayers, concluded that the chlorophyll in chloroplasts was amorphous. The granum has been recently described as a "soft" superlattice with a degree of local order, but lacking in precise long-range order (32). Chloroplasts, at least in some organisms, appear to be self-duplicating structures, and on this basis, many investigators suggest that they should contain nucleic acids. Stocking & Gifford (92) have recently reported that 80 to 90 per cent of the incorporated radioactivity of *Spirogyra* cells placed in solutions of tritiated thymidine appeared in the chloroplasts. Whether this indicates actual synthesis of nucleic acids by chloroplasts is not yet established.

The recent work on the structure of bacterial chromatophores has been reviewed by Frenkel (86) and by Bergeron (87). Newton & Newton (93) have carried out extensive studies on the chemical makeup of chromatophores. In most kinds of bacteria examined, the chromatophores were spherical vesicles a few hundred A in diameter (94). There were several thousand per cell, and they appeared only in light-grown cells. One aberrant case was that of the budding photosynthetic bacterium *Rhodomicrobium vanniellii* which was found by Vatter *et al.* (95) to possess concentric peripheral lamellae rather than chromatophores. However, Hickman & Frenkel (95a) showed that lamellae appeared in cells from old cultures of *Rhodospirillum rubrum*. Thus the morphology of photosynthetic organelles in bacteria may depend on the culture conditions. In some cases the chromatophores can be broken down to even smaller particles and still retain photochemical activity (86).

Bergeron (87), on the basis of size measurements and chemical analyses has proposed a model for the ultrastructure of chromatophores from the purple sulfur bacterium *Chromatium*. These chromatophores have an average diameter of 320 A and a molecular weight of about 13 million. Each chromatophore is estimated to contain 300 carotenoid molecules, 600 chlorophyll molecules, 3000 phospholipid molecules, and 400 protein molecules. Bergeron suggests that the above components are arranged in the form of a hollow sphere with an outer, 60 A thick, protein layer and an inner, 30 A thick, monolayer of phospholipid with the chlorophyll localized at the juncture of the two layers. Newton & Levine (96), using immunological techniques, have shown that *Chromatium* chromatophores contain polysaccharide components characteristic of the cell wall.

The Hill reaction.—The Hill reaction was reviewed in detail a few years ago by Lumry, Spikes & Eyring (97) and more recently by Clendenning (98) and by Whittingham (99). The Hill reaction of isolated chloroplasts provides an excellent system for precise kinetic studies because it does not exhibit the many transient phenomena characteristic of the complete photosynthetic process. Hill reaction studies can also be made using whole cells if

appropriate electron acceptors such as quinone are used. Some authors prefer to restrict the term "Hill reaction" to the isolated chloroplast reaction since the use of whole cells might permit the occurrence of other photochemical processes (99).

The precise relationship between the water-splitting mechanism of photosynthesis and that of the Hill reaction is not known; however, the kinetics of oxygen production is not identical in the two cases. The photochemical splitting (photolysis) of water has been regarded as the basic photochemical process in photosynthesis. In this process water is assumed to be split with the formation of a reduced product and an oxidized product. The latter then produces molecular oxygen by a series of unknown reactions, while the other product could be used for the reduction of carbon dioxide or of Hill reaction electron acceptors (oxidants). Warburg & Krippahl (100) reported that catalytic amounts of carbon dioxide were an absolute requirement for the Hill reaction. They interpreted this to indicate that the photolysis of water could not be the primary event in photosynthesis. This result has not been confirmed as yet (99). Arnon (101) recently proposed a master scheme for the reactions carried out by chloroplasts. He regards photosynthetic phosphorylation as the fundamental photochemical reaction, with oxygen evolution resulting from a non-photochemical process somewhat removed from the main reaction pathways. Jagendorf (102), however, suggests that the photolysis of water is the primary step in both the Hill reaction and photosynthetic phosphorylation. In spite of our lack of knowledge, the present authors feel that the Hill reaction still provides an interesting model system for studying the photochemical evolution of oxygen by photosynthetic organisms. Most of the older work on the Hill reaction must be re-examined, however, in view of recent work on the interactions between the Hill and phosphorylation reactions (101, 102).

A recurrent problem in studies of the chloroplast Hill reaction is the experimental material, i.e., the plant species used, the techniques used for the isolation and storage of the chloroplasts, etc. Clendenning (98) has recently reviewed the literature on chloroplast isolation and purification together with a consideration of the natural inhibitors in many plant cells, the storage and thermal deterioration of chloroplasts, and the effects of plant age on chloroplast properties. Environmental conditions (temperature, light intensity, photoperiod, nutrition, etc.) during plant growth have profound effects on chloroplast properties. Appleman & Pyfrom (103) have made the very interesting observation that chloroplasts from plants grown under red light had only 60 to 70 per cent of the Hill reaction activity on a chlorophyll basis as did chloroplasts from plants grown under blue light. The mechanism involved is unknown, although it was also noted that catalase activity in the plants was decreased by blue light and increased by red light. Chloroplasts are usually isolated in aqueous media, which results in the loss of water-soluble components. Stocking (104) isolated chloroplasts from lyophilized leaves using non-aqueous solvents. Such chloroplasts lacked photo-

chemical activity but did retain high activities of aldolase and phosphorylase, enzymes which are largely removed by the usual isolation techniques. Punnett (105) has recently made a detailed study of the stability of chloroplast preparations from a variety of plants. The stability varied widely with different species and apparently with different growth conditions. Whole chloroplasts were stabilized by glucose, whereas chloroplast fragments were stabilized by chloride. The Hill reaction activity was rapidly lost under conditions of high pH. Park & Pon (106) found that chloroplasts fragmented by sonication showed an increased ferricyanide Hill reaction rate. They interpreted this as indicating that the rate with intact chloroplasts is limited by availability of ferricyanide and that sonication removes the barrier to ferricyanide.

A suitable electron (or hydrogen) acceptor (oxidant) must be present in order for the Hill reaction to proceed to any appreciable extent, as shown in Equations 2 and 3. A variety of both physiological and nonphysiological oxidants with a wide range of redox potentials will function, including ferric salts, ferricyanide, a number of different quinones, redox dyes such as the phenolindophenols, chromate, molecular oxygen, cytochrome-c, DPN, TPN, riboflavin, FAD, etc. (97, 99). This low specificity with respect to structure and potential suggests that the oxidant is reduced by some very high energy intermediate (107). Most oxidants are reduced by highly washed chloroplast fragments, indicating that readily extractable enzymes and soluble cofactors are not generally involved. In the case of TPN reduction, however, San Pietro & Lang (108) have shown that a TPN-specific soluble enzyme from chloroplasts termed "photosynthetic pyridine nucleotide reductase" is required. San Pietro and co-workers (109) showed that the action spectrum for TPN reduction was very similar to the chloroplast absorption spectrum and to the action spectra for photosynthesis, the Hill reaction, and photosynthetic phosphorylation. They suggested that the primary photochemical process, photolysis, was the same for all of these reactions.

Marrè & Forti (110) found that illuminated chloroplasts continued to reduce TPN even when ATP synthesis was inhibited by dinitrophenol. They interpret this as indicating that TPN is reduced directly by the primary reducing agent in photosynthesis rather than indirectly through an ATP-dependent process. A protein ("haem factor") markedly accelerated the reduction of cytochrome-c in the Hill reaction with the production of rates of oxygen evolution well in the photosynthetic range (111). Krogmann & Jagendorf (112) showed that trichlorophenol indophenol was reduced several times faster than ferricyanide by freshly prepared spinach chloroplasts. Various treatments such as ageing, sonication, and dilution increased the rate of ferricyanide reduction. Krogmann & Jagendorf (113), incidentally, have described a useful spectrophotometric assay for the ferricyanide Hill reaction. Activity of chloroplasts from red kidney bean leaves was increased significantly by grinding the leaves in the presence of versene or at a high pH; activity was rapidly lost on sonication (114). Activity could not be increased

by versene once the chloroplasts were isolated. Marcus *et al.* (115) examined the absorption spectra of a large number of known and suggested oxidants and found that effective compounds, in general, absorbed light at the blue peak of chlorophyll whereas inactive compounds did not. If electronic excitation energy is transferred from chlorophyll to the oxidant in the Hill reaction, the Franck-Condon principle requires that the chlorophyll and oxidant have overlapping energy levels. They suggested that overlapping absorption bands could indicate overlapping energy levels, and that on this basis all Hill oxidants would show absorption in the blue. Using this rationale, Hatchett & Marcus (116) found cobaltioxalate, which absorbs at 420 mμ, to be a Hill oxidant. Taylor & Chessin (117) showed that isolated bean chloroplasts reduced blue tetrazolium. The dark blue, insoluble, reduction product was confined to the grana regions. In summary it should be pointed out that studies of the participation of the oxidant in the Hill reaction are complicated by the fact that many oxidants have secondary effects on the photochemical process (107); further, the reduction of some oxidants such as ferricyanide is closely coupled with photosynthetic phosphorylation [see (102) for discussion].

Extensive attempts have been made for many years to fractionate the chloroplast Hill reaction system, but without success. Finally, Lynch & French (118) made the extremely interesting observation that lyophilized chloroplasts lost Hill reaction activity when extracted with petroleum ether and that activity was restored by readdition of the extract. They reported that β-carotene was the active component in the extract; the extract, however, was more effective than the pure compound. Bishop (119, 120) reexamined this system and reported that vitamin K, not carotene, was the active material. More recently (121), he made the unexpected observation that chloroplasts did not contain vitamin K as previously reported and that the active compound was a benzoquinone (which he termed Q-255) apparently belonging to the recently discovered "ubiquinones" or "Q-coenzymes" involved in mitochondrial electron transport (122). The precise role of Q-255 in the Hill reaction is not known, although it may well participate in photosynthetic electron transport (32). Wessels (123), Arnon (101), and others have proposed mechanisms for vitamin K participation in photosynthesis; these considerations would apply equally well to the ubiquinones. Eversole & Wolken (124) and Wolken (81) reported that extracts of chloroplasts in 1 per cent digitonin, which they termed "chloroplastin," were able to reduce dye, evolve oxygen, and produce labile phosphate on illumination. The average molecular weight of chloroplastin was 40,000 and approximately one chlorophyll molecule was associated with each protein macromolecule. If photochemically active chloroplastins are a general phenomenon it will necessitate considerable revision of our ideas on photosynthesis; in particular, if separate entities containing only one chlorophyll molecule are functional, the concept of a photosynthetic unit would be meaningless. Further, if several quanta are required to split a water mole-

cule, the mechanism by which a chloroplastin molecule could accumulate sufficient quanta at low light intensities to provide the necessary energy would be intriguing!

A standard approach to the elucidation of complex biochemical reaction sequences is the use of selective inhibitors. It has been known for a long time, for example, that the carbon dioxide fixation part of photosynthesis is much more sensitive to cyanide than the oxygen-evolving part. The older work on inhibitors has been reviewed extensively (3, 97, 99). Of the newer inhibitors studied, the most interesting are a group of herbicides represented by 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU), and 3-(4-chlorophenyl)-1,1-dimethylurea (CMU), which were first shown by Wessels & van der Veen (125) to inhibit the Hill reaction at concentrations of approximately 10^{-7} M. Spikes (126) reported that the photochemical part of the Hill reaction was considerably more sensitive than the dark steps. DCMU also completely suppresses the Hill reaction at concentrations of one DCMU molecule per several hundred chlorophyll molecules, an observation which supports the concept of the photosynthetic unit. CMU and DCMU appear to be specific inhibitors for oxygen production in photosynthetic reactions. DCMU was shown by Bishop (127) to have no inhibitory effect on the photoreduction process of hydrogen-adapted algae; DCMU also prevented reversion to photosynthesis at high light intensities indicating that the effect was on oxygen evolution reactions. Another weed-killer, 2-chloro-4,6-bis-(ethylamino)s-triazine, also blocks the Hill reaction (128). This compound probably kills plants simply by preventing photosynthesis, since treated barley plants survived if fed with glucose. Krogmann & Jagendorf (129) found that fatty acids with chain lengths of 12 or more carbon atoms irreversibly inhibited the light process of the Hill reaction.

Manganese appears to play an essential role in the oxygen-evolving part of photosynthesis and the Hill reaction. Kessler (130) showed that manganese-deficient algae no longer produced oxygen; however, photoreduction was not altered appreciably. Eyster and co-workers (131) reported that the Hill reaction progressively fell to zero when plants were grown under manganese-deficient conditions. Addition of manganese to deficient cultures restored activity in a short time. *Chlorella* provided with just enough manganese to carry out normal rates of Hill reaction and photosynthesis had a molar manganese:chlorophyll ratio of 1:600.

Rieske, Lumry & Spikes (132) showed that the steady-state rate vs. light intensity relationship for the ferricyanide Hill reaction of washed chloroplast fragments was a rectangular hyperbola within narrow statistical limits. A rate law of this simple form imposes a number of restrictions on possible reaction mechanisms. On the basis of this rate law it was proposed that the trapping center of the photosynthetic unit behaved like a simple quenching agent for chlorophyll fluorescence. Further, it was proposed that the "finishing time" or "dark time" of the Hill reaction would result from a delayed regeneration of the center after trapping. Equations were derived

from these assumptions for predicting the relationship between fluorescence yield and exciting light intensity. It was shown by Mayne (42) and by Lumry, Mayne & Spikes (43) that experimental data on fluorescence yield fit these predictions reasonably well. On the basis of this work, Lumry & Rieske (133) developed formal mechanisms for the steady-state Hill reaction under a variety of conditions. Thomas & Nuboer (134) found that plants with grana chloroplasts have a shorter fluorescence induction period than those with lamellar chloroplasts. They interpreted this result as indicating that photosynthetic enzymes and cofactors are located in part in the stroma region of the chloroplast.

Photosynthetic phosphorylation.—Without question, the single most important discovery with respect to the mechanism of photosynthesis since the last review in this series was that of photosynthetic phosphorylation. Many workers [see (102) for references] have suggested that high-energy phosphates such as ATP would be formed during photosynthesis. It was not until six years ago, however, that this was demonstrated experimentally by Arnon, Whatley & Allen (135) using spinach chloroplasts and by Frenkel (136) working with subcellular particles from the photosynthetic bacterium *Rhodospirillum rubrum*. Because of its extreme importance in the understanding of energy transport in the photosynthetic process, photosynthetic phosphorylation has been one of the most popular and active areas of research during the past few years. Its popularity was enhanced because of possible similarities to oxidative phosphorylation in which mitochondria synthesize ATP using energy from the oxidative breakdown of organic compounds [see (137)]. A detailed discussion of photosynthetic phosphorylation is beyond the scope of this review. There is general agreement about much of the experimental data, but considerable disagreement on some details, especially on the integration and interpretation of information. Fortunately there are excellent recent reviews by Jagendorf (102, 138) and by Arnon (101, 139), which provide detailed information and interpretation as well as references.

Cyclic photosynthetic phosphorylation as shown in Equation 4 was the first type observed with chloroplasts (101). This reaction requires chloroplasts, ADP, magnesium ion, and catalytic amounts of some redox cofactor. Maximum rates occur at a magnesium : ADP ratio of 2 (140). Since the cofactor requirement is rather unspecific, all of the electron-transfer reactants, enzymes, etc. of real importance in the cycle must be bound up in water-insoluble forms within the chloroplast. As Lumry & Spikes (32) stressed recently, our greatest need for information in photosynthesis is on the biochemistry and molecular chemistry of these "fixed" chloroplast reactants since, at present, we know essentially nothing about the numbers, kinds, sequences, etc. of electron-transfer processes within the chloroplast. If chloroplastin (124) carries out photosynthetic phosphorylation it should be investigated for its mechanism because of its simplicity. At present our best experimental approach is probably to study the kinetics of electron

flow through added Hill reaction agents and cofactors, in the hope that we can thus indirectly gain information concerning the internal pathways. A wide variety of cofactors function in cyclic photosynthetic phosphorylation, including riboflavin (141); K vitamins (142); various dyes such as phenazine methosulfate, pyocyanine, indigo carmine, and methyl viologen; etc. (143, 144). These cofactors do not all show the same kinetic behavior. Arnon & co-workers (101, 145) concluded that there were two kinds of chloroplast cyclic photosynthetic phosphorylations. They termed these the riboflavin phosphate (FMN) pathway, which requires TPN and chloride, and the vitamin K pathway [also see (146)]. These conclusions are not shared by all workers in the field. It is probably safest to say at present that considerable additional data will be required to delineate the possible alternate pathways in chloroplast cyclic photosynthetic phosphorylation [see (144)].

Arnon and co-workers (139) discovered a non-cyclic type of photosynthetic phosphorylation with chloroplasts in which ATP was synthesized, TPN was reduced, and molecular oxygen was evolved, with the stoichiometry indicated in Equation 5. Since TPNH and ATP are required for carbon dioxide reduction, and since molecular oxygen is evolved in the photosynthesis of the algae and higher plants, the reaction given in Equation 5 may well be an integral part of whole-cell photosynthesis [also see (147)]. An analogous reaction with ferricyanide rather than TPN was also observed (139). Jagendorf, Avron, Krogmann, and co-workers, in an extensive series of studies [see (102) and (148)], have examined the kinetics of the non-cyclic reaction in detail. They found that phosphorylation was tightly coupled to ferricyanide reduction in that the rate of ferricyanide reduction increased several fold when phosphorylation was permitted to occur simultaneously by the addition of magnesium ion, inorganic phosphate, and ADP. The rate of TPN reduction, however, was not increased by permitting phosphorylation to occur, and when certain other oxidants such as 2,3,6-trichlorophenol-indophenol were used, phosphorylation did not occur at all (112). Thus, all possible situations were represented, i.e., tight coupling, loose coupling, and a complete lack of coupling between phosphorylation and electron flow to the oxidant. Jagendorf and co-workers made a search for treatments that would permit maximal electron flow to the oxidant in the absence of phosphorylation. Three methods for such an uncoupling were found; dilution of the chloroplasts with $0.35M$ sodium chloride at pH 6 (112), addition of ammonium ion (149), and the replacement of phosphate by arsenate (102). Wessels (150) recently reported that dinitrophenol accelerated ATP synthesis by illuminated chloroplasts. Whether this bears any relation to its uncoupling action in oxidative phosphorylation is not known.

Another type of reaction termed "oxygen-catalyzed" or "oxidative" photosynthetic phosphorylation also occurs [see (151) for a literature review]. In this reaction chloroplasts, in a system containing inorganic phosphate, ADP, and an appropriate redox dye, synthesize ATP on illumination in the presence of oxygen, but not in its absence. The mechanisms involved

in this process and its relationship to the other types of phosphorylation described above are not clear, however, it will very likely provide another useful approach to the elucidation of photosynthetic phosphorylation.

There are a number of proposed reaction schemes to account for the processes carried out by isolated chloroplasts. Arnon (101), summarizing the ideas of his research group, envisions that electrons in chlorophyll are raised to high energy levels by absorbed quanta. These electrons flow back to chlorophyll via reaction paths in which ATP is synthesized through cytochrome-coupled reactions. In non-cyclic phosphorylation, electrons from chlorophyll would be transported to TPN and then replaced by electrons from OH radicals via cytochromes with the resulting evolution of oxygen. Direct experimental evidence is not available for all of these proposed reaction steps.

Jagendorf (102) summarized the work of the Johns Hopkins group using the assumption that, upon illumination, photosynthetic organelles split some compound, probably water, with the production of oxidizing and reducing intermediates. In cyclic photosynthetic phosphorylation the added redox cofactor permits the electron flow which results in the regeneration of the split compound and the synthesis of ATP. Also, one intermediate could oxidize exogenous compounds while the other could reduce another compound, as in bacterial photosynthesis. Support for this concept is provided by Vernon & Hobbs (152) who showed that isolated chloroplasts capable of carrying out the conventional Hill reaction could also, photochemically, both oxidize ascorbate and reduce the dye indigo carmine [see also (153, 154)]. Marrè & Arrigoni also examined chloroplast-ascorbic acid redox reactions (155). Jagendorf (102) presented an integrated scheme that summarizes the kinetics of the Hill reaction, cyclic photosynthetic phosphorylation with different cofactors, and non-cyclic photosynthetic phosphorylation with TPN and ferricyanide.

Reactions of bacterial chromatophores.—Frenkel (86) has recently reviewed the photochemical reactions of isolated chromatophores. Bacterial photosynthetic phosphorylation, which is of the cyclic type, requires chromatophores, ADP, magnesium ions and catalytic amounts of some non-specific reducing material such as succinate, reduced DPN, etc. (156). With chromatophores, unlike chloroplasts, electron flow can apparently occur via endogenous materials, perhaps through cytochrome-c_2, a special cytochrome characteristic of photosynthetic bacteria, as indicated by the work of Smith & Baltcheffsky (157). Newton & Kamen (158) suggested that the added reducing material is necessary to poise the internal redox system of the chromatophores at a potential permitting maximal electron flow. The work of Anderson & Fuller (159) supports this view. Arnon and coworkers reported that bacterial chromatophores have only the "vitamin K" pathway of photosynthetic phosphorylation (101). Anderson et al. (160) showed that light absorbed by the carotenoids in the chromatophores of the

photosynthetic, purple, sulfur bacterium *Chromatium* supported photosynthetic phosphorylation if the chromatophores were isolated in an appropriate buffered sucrose medium. The energy transfer from carotenoids was uncoupled from phosphorylation in other isolation media; the carotenoids continued to protect the bacteriochlorophyll from photooxidation even when uncoupled. Possible mechanisms for this phenomenon were discussed by Bergeron (87). Goedheer, however, on the basis of measurements of the action spectrum of fluorescence, found no differences in energy transfer from carotenoids to bacteriochlorophyll in *Rhodospirillum rubrum* and *Rhodopseudomonas spheroides* using intact bacteria and chromatophores prepared in a variety of media (161). Photooxidation reactions of isolated chromatophores from *Rhodospirillum rubrum* have been recently re-examined by Vernon and co-workers (162, 163).

Carbon dioxide fixation by chloroplasts.—Arnon and co-workers (135) were probably the first to regard the chloroplast as the site of photosynthetic carbon dioxide fixation, and a series of papers from Arnon's laboratory (101, 139, 164, 165) demonstrated that the products of carbon dioxide fixation by isolated chloroplasts were similar to those produced by intact cells (7), although the rates of fixation were much lower. However, Thomas *et al.* (166) reported that fragmented chloroplasts from the alga *Spirogyra* reduced carbon dioxide at about the same rate as intact cells.

Gibbs & Cynkin (167) found that the labeling of glucose produced by the photosynthesis of isolated spinach chloroplasts showed the same asymmetry as that produced by whole cells. Gibbs & Calo (168) examined the effects of a number of factors, including inhibitors, on the photosynthetic carbon dioxide fixation by isolated spinach chloroplasts. Holm-Hansen *et al.* (169), working with spinach, found that both chloroplasts and sap fixed carbon dioxide; the rate of fixation by a chloroplast-sap mixture was greater than the sum of the separate rates. Chloroplast fixation produced primarily phosphate esters, while sap fixation resulted mainly in amino acids. Even under optimal conditions the chloroplasts fixed carbon dioxide at only about 1 per cent the rate, on a chlorophyll basis, as that in whole cell photosynthesis, although rates of oxygen evolution and photosynthetic phosphorylation are about the same in the two cases. Park *et al.* (88) showed that chloroplast particles as small as 0.1 micron and containing as few as 50,000 chlorophyll molecules fixed carbon dioxide as rapidly as whole chloroplasts. Trebst and co-workers (170) showed quite clearly that the photosynthesis of isolated chloroplasts could be separated into a light and a dark phase. The carbon-dioxide fixing enzyme systems were not too firmly bound to the chloroplasts and could be extracted without interfering with the photosynthetic phosphorylation reaction of the chloroplasts. The extract would fix carbon dioxide in the dark into the same products found in photosynthesis if ATP and TPNH were added in appropriate amounts. Irmak (171) showed that destarched tobacco chloroplasts produced essentially normal starch

grains on illumination, but not in the dark, while Ueda studied photosynthetic starch formation in *Elodea* chloroplasts as isolated in various ways (172).

Chloroplast reactants other than chlorophyll.—Some enzymes are concentrated in the chloroplasts; also, a number of specialized enzymes for the synthesis of the pigments and other chloroplast constituents must be present. Since chloroplasts carry out carbon dioxide fixation, photosynthetic phosphorylation, and oxygen evolution, the extensive array of enzymes necessary for these processes must also be present. Research on the enzymology of plastids is of obvious importance in elucidating the chemical pathways in photosynthesis and in understanding chloroplast-cytoplasm interactions. This important area of work will not be considered further here, but fortunately there is a recent detailed review on plastid enzymology by Sissakian (173). Many of the functional components of the chloroplast are firmly bound into its structure. Thus, as in mitochondria (137), the organization and arrangement in space of the fixed reactants of the chloroplast are intimately involved in the reactions carried out. These processes, which apparently take place in a heterogeneous system, are likely to be rather different from analogous processes occurring in solution.

Carotenoids are of universal occurrence in photosynthetic structures in nature. Although light energy absorbed by carotenoids can be transferred to chlorophyll and used for photosynthesis by some organisms, no general function has been attributable to the carotenoids. Recent studies with mutant photosynthetic bacteria lacking carotenoids and with cultures in which carotenoid synthesis was suppressed with diphenylamine showed that, in the absence of carotenoids, cells were rapidly damaged and killed in the light by chlorophyll-sensitized photooxidation processes [see (83, 174)]. Isolated carotenoid-depleted chromatophores were also photosensitive in the presence of oxygen (175). The mechanism of protection by carotenoids has not been established. However, carotene is an excellent quencher for the chlorophyll triplet state (22). Thus, an important function of carotenoids in plants might well be to quench the chlorophyll triplet state in competition with molecular oxygen and thus prevent injurious photooxidation reactions (32). Carotenoids might also play a chemical role in photosynthesis. "Carotene-free" photosynthetic bacteria photosynthesize (83, 174), and Bishop (119) showed that extraction of carotenoids did not interfere with chloroplast Hill reaction activity. However, in both cases enough carotenoid might remain to provide a minimum of one molecule per trapping center. Blass *et al.* (176) observed light-dependent carotenoid interconversions, and certain of the spectral changes observed with photosynthetic bacteria and algae on illumination may be due to changes in carotenoids [reviewed in (177)]; thus oxidation-reduction reactions of carotenoids may be involved in photosynthesis. It has been suggested that carotenoids could provide a site for the dismutation of water molecules in photosynthesis through endo-peroxide

formation (3, 27, 32). Platt (178) recently presented a more elegant treatment of earlier suggestions that carotenes function as "electron pipelines" in channeling electrons in photosynthesis. He suggested that if appropriate electron donors and acceptors are positioned at opposite ends of carotenoid molecules the carotenoid would act as a site of charge displacement and thus allow simultaneous oxidations and reductions. Goodwin (179) has recently published an extensive general review on the structure, distribution, biosynthesis, and function of carotenoids in plants.

During the past few years it has become apparent that cytochromes are probably intimately involved in electron transport in the photosynthetic process, even in strictly anaerobic organisms where molecular oxygen is not involved. Higher plants contain cytochromes a_3, b, b_3, c, b_6, and f [see (2)]. The first four occur throughout the plant, while cytochromes f and b_6 are confined to the chloroplasts where they amount to as much as 20 per cent of the total chloroplast protein. Vernon & Kamen [reviewed in (180)] showed that photosynthetic bacteria contain large amounts of "modified" c cytochromes. Davenport & Hill (181) suggested that, because of its high redox potential, cytochrome-f might function in the energy transport processes of photosynthesis, while Vernon & Kamen (180) suggested that the specialized cytochromes in photosynthetic bacteria might play an analogous role. Duysens first demonstrated that cytochromes were oxidized during photosynthesis on the basis of certain spectral shifts in photosynthetic bacteria on illumination (182). More recently, various workers have reported that cytochrome-f is oxidized upon illumination of green and red algae, isolated chloroplasts, and leaves [reviewed in (183)]. Further, cytochrome-c_2 is oxidized photochemically, but not by oxygen in *Rhodospirillum rubrum* (157). There is some difference of opinion in this field since the measurements are difficult to make. It is probably best to say, then, that cytochromes are very likely involved in photosynthesis, but that as yet we know few of the details. Little is known of the "state" of the cytochromes in the chloroplast, except that cytochrome-f cannot be extracted with aqueous solvents; treatment with organic solvents is necessary. Kamen (180) pointed out that the cytochromes resemble chlorophyll closely enough that they might be excited directly by inductive resonance. The cytochromes thus might be localized in the protein region of the lamellae in close proximity to the porphyrin heads of the chlorophyll molecules so that excitation energy would migrate through chlorophyll to cytochromes where the quantum conversion process could occur, i.e., the cytochromes might be involved directly in the trapping center. Recently, Duysens and co-workers (184, 185) have developed fluorescence action spectrum techniques for measuring changes in pyridine nucleotides in photosynthesizing cells. Apparently reduced pyridine nucleotide is formed in illuminated cells and chloroplasts with efficiencies and rates sufficient to account for an appreciable fraction of the carbon dioxide fixed in photosynthesis.

BIOCHEMISTRY OF PHOTOSYNTHETIC REACTIONS

In the overall photosynthetic process of higher plants and algae, carbon dioxide and water are utilized and organic compounds and molecular oxygen are produced as shown in Equation 1. The pathways by which the carbon of carbon dioxide is converted into organic compounds are fairly well understood, but we know very little concerning the pathways of hydrogen and of oxygen in photosynthesis. In the space available we will attempt to give a very brief picture of the present status of these areas of research.

Pathway of carbon in photosynthesis..—This field has been recently described in a monograph by Bassham & Calvin (7) and in a detailed review by Vishniac *et al.* (186). In photosynthetic carbon dioxide fixation it will be recalled (based largely on the work of Calvin, Benson, Bassham, and coworkers) that the 5-carbon compound ribulose diphosphate combines with carbon dioxide to form two molecules of 3-phosphoglyceric acid (PGA). The PGA is then reduced to triose phosphate with energy obtained from light. Some of the triose phosphate is used via complex pathways for the regeneration of ribulose diphosphate, while some is used for the synthesis of fructose, sucrose, etc. The fixation of one molecule of carbon dioxide is estimated to require two molecules of TPNH and three molecules of ATP (7). Not all of these proposed steps are unequivocally established. For example, Gibbs & Kandler (187) have found that the glucose isolated from the starch and sucrose produced in short-term photosynthesis by *Chlorella* and leaves of higher plants is labeled asymmetrically. This would not be expected if hexose phosphate was produced by combining two similar triose phosphate molecules. Kandler (188), using a cyanide-inhibition technique, postulated a pathway in which the ribulose carboxylation product is converted to fructose via a polyhydroxy acid. Thus, pathways for carbon dioxide fixation could occur in which PGA would not be a precursor of hexose. These results are supported by the recent work of Mortimer (189) on the carbon dioxide fixation by leaves of sugar beet and soy bean in which only very small quantities of PGA are produced. Bassham & Kirk (190), by measuring the concentrations of intermediates during steady-state photosynthesis in *Chlorella*, found that the Calvin cycle accounts for at least 80 per cent of the carbon dioxide fixed under the conditions used. Vejlby (191) has attempted to explain the induction phenomenon in photosynthesis in terms of the relative amounts of carbon dioxide acceptor in the plant in the light and in the dark. Plant leaves fix considerable quantities of carbon dioxide in the dark into organic acids and amino acids; phosphorylated sugars and other carbohydrates do not appear (192). Warburg & Krippahl (193) described experiments on a fluoride-produced "carbon dioxide gush" from algae which they interpreted as indicating that carbon dioxide fixation in photosynthesis proceeded via a stable chlorophyll-carbon dioxide complex, a hypothesis first proposed by Willstäter and Stoll in 1918. Bishop & Gaffron (194) presented data opposed to this interpretation and suggested that the gush probably resulted from the decarboxylation of an organic acid. Warburg *et al.* (195) later re-

ported the gush to result from the decarboxylation of glutamic acid; therefore, at present there seems to be little support for the old Willstäter-Stoll hypothesis. Warburg has recently reviewed the overall contributions of his laboratory to the field of photosynthesis (12). Voskresenskaya & Grishna (196) reported that some plants preferentially synthesize carbohydrate in red light and protein in blue light. Cayle & Emerson (197), working with *Chlorella*, did not obtain this result. They did find, however, that the specific activity of the amino acids was almost twice as great after photosynthesis in blue light as compared to red. Roux *et al.* (198) have observed that the time-course of incorporation of radioactivity into different groups of organic compounds in leaves grown in radioactive carbon dioxide is influenced by the color of light used. Tamiya *et al.* (199) pointed out the importance of growth conditions in the study of *Chlorella* photosynthesis, especially from the point of view of the life-cycle stage involved. It seems obvious from the above, that whenever possible research in photosynthesis must be carried out with plants raised and studied under precisely controlled environmental conditions.

In summary, although considerable work remains to be done, it would appear that the major pathways of carbon flow in the photosynthetic process have been blocked out. One of the most promising approaches appears to be the precise determination of the rate of flow of carbon through each proposed intermediate compound by measuring their rates of labeling and steady state concentrations simultaneously under a variety of conditions (190). The role of compounds, in addition to those in the Calvin cycle, should be examined. For example, Benson and co-workers (200, 201) have examined the pathways for the photosynthesis of lipids in plants and have shown that such materials as the phosphatidyl glycerols, galactolipids, and sulfolipids are among the earliest compounds formed. Another promising area of research will probably be the study of the path of carbon in the photosynthetic bacteria. Stanier *et al.* (202) have recently re-examined the role of the organic substrate required in the photometabolism of many types of purple photosynthetic bacteria. It appears that the older concept of the organic material serving as a hydrogen donor for the reduction of carbon dioxide does not hold for most of the purple bacteria. Instead, the organic substrate serves largely as a readily available source of carbon.

Pathway of hydrogen in photosynthesis.—As may be seen in Equation 1, the hydrogen in the organic compounds synthesized by higher plants must come from water. Relatively little is known of the biochemical pathways involved, however. Weinberger & Porter (203) found that *Chlorella* incorporated deuterium only 50 per cent as rapidly as hydrogen, and tritium only 90 per cent as rapidly as deuterium. However, cells continued to grow very slowly even in 94 per cent deuterium oxide. Tritium and deuterium were incorporated into the lipid fraction to a much greater extent than into the protein, nucleic acid, and starch fractions. Moses *et al.* (204) reported that *Chlorella* could be adapted to grow to some extent in deuterium oxide

concentrations as high as 99 per cent, however, growth was slow and erratic. It is interesting to speculate on the possible alterations of structure in proteins and nucleic acids incorporating large fractions of deuterium, since hydrogen bonding is so important in maintaining the tertiary structure of such macromolecules and since the hydrogen bonds formed by deuterium differ in energy from those formed by protons. Walker & Syrett (205) made the interesting observation that, while autotrophic growth of *Chlorella* was inhibited almost completely in 90 per cent deuterium oxide, growth on glucose in both light and darkness continued at a reasonable rate, although the rate was slower in the light. Strain *et al.* (206) found that all of the photosynthetic pigments were present in algae raised in high concentrations of deuterium oxide. Crespi *et al.* (207) reported that adapted *Scenedesmus* grew sufficiently well in 99.6 per cent deuterium oxide to make the algae a practical source of essentially fully deuterated compounds.

San Pietro & Lang (208) showed that deuterium was transferred from deuterium oxide to pyridine nucleotides when these were reduced in the Hill reaction. Vischniac & Rose (31) found that part of the chlorophyll in algae, isolated chloroplasts and isolated *Chromatium* chromatophores became radioactive upon illumination in tritiated water. They suggested that the first step in the hydrogen transfer reaction chain in photosynthesis might be from water to chlorophyll. They also found a light-produced transfer of tritium from labeled chlorophyll to TPN in the presence of an acetone powder of spinach chloroplasts. Moses & Calvin (209) examined the light-produced incorporation of tritium from tritium oxide into organic compounds by *Chlorella*. Tritium appeared in essentially the same compounds as those incorporating radioactivity from radioactive carbon dioxide but the relative distribution was different. Relatively high rates of non-specific hydrogen-tritium exchange reactions made the interpretation of results considerably more difficult than with radioactive carbon. In summary, relatively little is known of the pathways of hydrogen metabolism in photosynthesis. However, in spite of the inherent difficulties, studies with deuterium and tritium should ultimately lead to valuable information.

Pathway of oxygen in photosynthesis.—The source of the molecular oxygen produced in photosynthesis is obviously water and/or carbon dioxide. Although there are theoretical reasons for expecting all of the evolved oxygen to be derived from water, isotopic experiments do not establish this result unequivocally (210). Most workers in photosynthesis, however, seem to operate on the assumption that all of the oxygen does come from water. Nothing is known of even a single intermediate in the oxygen evolution reactions. Dorough & Calvin (211) suggested that oxygen might be produced through the hydration of a double bond on a carotenoid followed by oxidation to an epoxide; the removal of oxygen would then restore the original pigment structure. Experiments using water enriched with oxygen-18 were inconclusive. Sapozhnikov *et al.* (212) reported that xanthophyll was converted to a related diepoxide, violaxanthin in the dark, while the reverse

process went on in the light. More recently, Blass *et al.* (176) also observed a depression of the violaxanthin concentration in the light and suggested that one mechanism for this process would involve the photochemical production of molecular oxygen from the violaxanthin. Fögelstrom-Fineman *et al.* (213) carried out preliminary studies with an interesting activation technique for following the path of oxygen in photosynthesis. Algae were permitted to photosynthesize in water enriched with oxygen-18. Extracts of the algae were chromatographed, and the oxygen-18 activated to fluorine-18 by bombardment with 4.5 Mev protons. The radioactive fluorine-18 can then be readily located with radioautographic techniques. Preliminary experiments showed three photosynthetic products containing oxygen-18 from the water. These were located in the areas of the chromatogram corresponding to sugar phosphates and PGA. Mason (214), in a review on the biological reactions of molecular oxygen, suggested that some of these reactions acting in reverse might provide interesting model systems for the photosynthetic production of molecular oxygen.

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